ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

POLYURETHANE MODIFICATIONS via DOUBLE CLICK REACTIONS

M.Sc. THESIS

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Department of Chemistry

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İKİLİ "CLİCK" REAKSİYONLARI İLE POLİÜRETAN MODİFİKASYONU

YÜKSEK LİSANS TEZİ

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Erhan DEMİREL, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **509131011**, successfully defended the **thesis** entitled "**POLYURETHANE MODIFICATIONS via DOUBLE CLICK REACTIONS**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my beloved family,

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December 2014

Erhan DEMİREL
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ABBREVIATIONS

λ	**:** Wavelength
nm	**:** Nanometer
C	**:** Concentration
k_{act}	**:** Activation rate constant
k_{deact}	**:** Deactivation rate constant
°C	**:** Celsius
^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
^{19}F NMR	**:** Fluorine Nuclear Magnetic Resonance Spectroscopy
GPC	**:** Gel Permeation Chromatography
UV	**:** Ultra Violet
TEA	**:** Triethylamine
THF	**:** Tetrahydrofuran
PU	: Polyurethane

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POLYURETHANE MODIFICATIONS via DOUBLE CLICK REACTIONS

SUMMARY

Polyurethanes (PU) discovered by Otto Bayer in 1937 and has gained grate importance since the discovery. PUs are employed in a broad range of uses and applications, including machinery, transport, furnishing, textiles, paper-making, packaging, adhesives, sealants and medicine. In addition, the outstanding mechanical properties and biocompatibility of the polyurethanes makes them some of the most promising synthetic biomaterials. PUs comprise three monomers: a diisocyanate, a macroglycol (which is an oligomeric monomer), which possess more complex chemical structures than other available polymers. By selecting the type of isocyanate and polyols, or combination of these groups, one can design the structure to obtain desired physical and chemical properties. Many different modification methods are used for modification of polyurethanes but among them click chemistry is the most versatile pathway for synthesis of polymeric structures.

In 2001, Sharpless and coworkers introduced "click" chemistry, a new approach in organic synthesis that involves a collection of almost perfect chemical reactions. Nowadays there are several processes have been identified under this term in order to meet Sharpless's criteria. Among those selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC), active ester substitution reactions and Diels-Alder (DA) cycloaddition reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists.

CuAAC reaction is a virtually quantitative, very robust, insensitive, general, and orthogonal ligation reaction between organic azides and alkynes. When compared with Huisgen 1,3-dipolar cycloaddition reaction, the copper catalyzed reaction allows to proceed much faster under much milder conditions and produces only one isomer which is 1,4-regiosomer triazole. In fact, the discovery of Cu (I) as catalyst has a great importance which efficiently and regiospecifically combines terminal alkynes and azides under mild conditions.

Diels-Alder (DA) reaction is one of the most common reactions used in organic chemistry, and invented by Otto Diels and Kurt Alder who received the Nobel Prize in 1950 for their discovery. The Diels-Alder reaction is a concerted [$4\pi+2\pi$] cycloaddition reaction of a conjugated diene and a dienophile to yield a 6-membered ring. This reaction is one of the most powerful tools used in the synthesis of important organic molecules in high yields.

In addition to CuAAC and DA reactions, active esters are famous in the field of peptide synthesis in organic chemistry. This methodology has been much applied mainly to form peptide bonds under mild conditions in both liquid and solid phase synthesis. Many different active esters have been presented but among them perfluorophenyl esters gained great interest in polymer chemistry. These reactive groups can be

transformed into amide groups by polymer analogous reaction with primary or secondary amines in a quantitative and simple way.

In this study, different PUs were prepared with pendant functional groups suitable for click chemistry to modify PUs with highly efficient click reactions. After polymerization of hexamethylene diisocyanate with three different functional diols consisting alkyne, anthracene and perfluorophenyl ester functional groups PU-(anthracene-*co*-alkyne) and PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) were obtained. PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) was reacted with azide, maleimide and amine functional compounds using CuAAC, active ester substitution reaction and DA reaction respectively. PU-(anthracene-*co*-alkyne) first studied as model reactions with small molecules to determine CuAAC and DA reaction efficiency. Next, CuAAC and DA reaction were employed to obtain PU-*g*-(PEG-PMMA) by reacting azide end functional polyethylene glycol and maleimide end functional poly(methyl methacrylate) respectively. The UV, NMR and GPC measurements revealed that CuAAC, Diels-Alder and active ester substitution reactions displayed an efficient and an alternative pathway for modification of PUs.

İKİLİ "CLICK" REAKSİYONLARI İLE POLYÜRETAN MODİFİKASYONLARI

ÖZET

Poliüretanlar ilk olarak Otto Bayer tarafından 1937 yılında bulunmuş ve II. Dünya Savaşı ve sonrasında büyük önem kazanmıştır. Poliüretanların keşfi sonrasında yapılan çalışmalar sonrasında pek çok alan ve uygulamada kullanılmaya başlanmıştır, örneğin otomotiv, tekstil, kağıt, paketleme sanayinde, paketleme malzemelerinde ve ilaç sanayinde kullanım alanı bulmuştur.

Endüstriyel olarak üretilen polimerlerin çoğu kabaca basit kimyasal yapılara sahipken poliüretanlar üç farklı monomer kullanılarak üretilebildiğinden kompleks yapıların sentezine imkan vermektedir. Poliüretan yapı taşları diisosiyanatlar, polioller ve zincir uzatıcılar olarak sıralanabilir. Bu üç bileşen oluşturulacak sonuç polimerin fiziksel ve kimyasal özelliklerini belirleyecek şekilde seçilebilmekte ve istenilen özellikte poliüretanlar elde edilebilmektedir. Poliüretanlar yapı taşlarından kazandıkları fiziksel ve kimyasal özelliklerin haricinde ana zincirleri üzerinde taşıdıkları üretan bağı sayesinde zincirler arasında ve/veya farklı gruplarla hidrojen bağı kurarak farklı özellikler gösterebilmektedirler.

Poliüretanlar pek çok farklı yöntem ile türevlendirilmeye çalışılmıştır, fakat bu yöntemlerin arasında en ilgi çekeni "click" kimyasıdır. 2001 yılında Sharpless ve çalışma arkadaşları "click" kimyası başlığı altında organik sentezler için neredeyse mükemmel kimyasal reaksiyonlar koleksiyonunu içeren yayınlarını yayınlamışlardır. Sharpless "click" kimyasını istenen yapının hızlı ve güvenilir bir yol ile birbirleri ile birleştirerek elde edilesi olarak açıklamıştır. "Click" kimyası ilk olarak sentetik kimyada daha sonraları polimer ve malzeme biliminde son derece popüler bir evrensel araçlar haline gelmiştir. Günümüzde hala yaygın olarak kullanılmakta olan "click" kimyası, pek çok farklı yapıda organik bileşiklerin ve fonksiyonel polimerlerin sentezine kolaylık sağlayacak bir kapıyı aralamıştır.

Bunun ilaveten Sharpless, farklı reaksiyonların "click" reaksiyonları olarak tanımlanabilmesi için bu reaksiyonların yerine getirmesi gereken bir takım kriterler de sıralamıştır. "Click" kimyası içerisinde her ne kadar çok sayıda reaksiyon bulunsa da bu reaksiyonların arasında Cu (I) katalizörlüğünde azit-alkin siklokatılma reaksiyonu (CuAAC), Diels-Alder (DA) reaksiyonu ve aktif ester sübstitüsyon reaksiyonu son derece güçlü araçlar olarak dikkat çekmektedir.

Organik azitler ve alkinler arasında gerçekleşen reaksiyon yüz yıldan fazla bir süredir bilinmektedir. Buna rağmen bu reaksiyon Huisgen ve çalışma arkadaşları tarafından ancak 20. yüzyılın ortalarında detaylı olarak incelenmiştir. Huisgen'nin organik azitler ve alkinler arasında gerçekleşen 1,3-dipolar siklo katılma reaksiyonu organik kimya reaksiyonları arasında önemli bir yer tutmaktadır.

Isı ile gerçekleşen 1,3-dipolar katılması "click" kimyası koşullarını yerine getirememektedir; verimin düşük olması, oluşan ürünlerin yapı izomeri karışımları halinde elde edilmesi ve reaksiyonun yüksek sıcaklıkta gerçekleşmesi bu durumun sebeplerindendir. Isı ile gerçekleşen 1,3-dipolar katılması ile kıyaslandığında Cu (I) katalizörlüğünde gerçekleşen CuAAC reaksiyonu ısı ile gerçekleşen reaksiyona nazaran üstün özellikler göstermektedir. Cu (I) katalizörlüğündeki reaksiyon oldukça hızlı gerçekleşirken, reaksiyon ılımlı koşullarda ilerleyebilmekte ve tek bir yapı izomeri oluşturmaktadır. Bu reaksiyonun çok tercih edilmesinin sebebi reaksiyon şartlarının basit olması, yan ürün olmaması, verimin yüksek olması ve saflaştırmanın kolay olmasıdır. Gösterdiği bu üstün özellikler sayesinde CuAAC reaksiyonu "click" reaksiyonlar arasında önemli bir yere sahiptir.

Aktif ester reaksiyonları organik kimyada peptit sentezinde yaygın olarak kullanılmaktadır. Bu yöntem ılımlı koşullarda peptit bağlarının oluşturulabilmesi için hem sıvı hem de katı faz sentezlerinde geniş bir uygulama alını bulmuştur. Pek çok farklı aktif ester günümüzde kullanılmaktadır ancak perflorofenil esteri bunların arasında dikkat çekmektedir.

Fonksiyonel polimerler genellikle istenilen fonksiyonu taşıyan monomerlerin polimerleştirilmesi ile elde edilir, bu monomer ve/veya polimerlerin sentezlenmesi sentez aşamasında büyük sorunlar oluşturmaktadır. Seçilen fonksiyonun korunarak işlem sonrasında korumanın kaldırılması kullanışlı bir yöntem gibi dursa da koruma-korumanın kaldırılması işleminin pek çok dezavantajı bulunmaktadır. Kullanım zorluklarının bulunması sebebi ile alternatif yollar aranmış ve aktif ester reaksiyonları kullanışlı bir araç olarak görülmüştür. Yukarıda belirtildiği gibi aktif esterlerin pek çok üstün özelliği ideal bir başlangıç malzemesi olarak kullanılmalarına imkan sağlamaktadır, çünkü bu reaktif gruplar istenildiğinde kolayca primer ve sekonder aminler ile reaksiyona girerek amit gruplarına dönüştürülebilmektedir. Gösterdikleri özellikler sayesinde aktif esterler polimer kimyası alanında yaygın olarak kullanılmaya başlanmıştır.

"Click" reaksiyonları arasında büyük önem taşıyan bir diğer reaksiyon ise Diels-Alder reaksiyonudur. DA reaksiyonu konjuge bir dien ile bir dienofil arasında gerçekleşen [4+2] siklokatılma reaksiyonudur. Otto Diels ve Kurt Alder tarafından 1928 yılında keşfedilen reaksiyon, 1950 yılında Nobel ödülünü kazanmalarını sağlamıştır.

Siklokatılma reaksiyonu sonrası oluşan altı üyeli halkanın oluşum enerjisinin düşük olması, oluşan bu halkanın ısı uygulanarak parçalanıp bileşenlerine ayrılabiliyor olması DA reaksiyonlarının polimer kimyası alanında geniş bir kullanım alanı bulmasını sağlamıştır. Keşfinden itibaren artan bir ilgi ile kullanılan DA reaksiyonları günümüzde geniş bir kullanım alanı bulmuştur. Pek çok farklı moleküler yapıda polimerin sentezi DA reaksiyonlarının kullanılması sayesinde başarı ile gerçekleştirilmiştir.

Poliüretanların modifikasyonunda pek çok farklı yol ve metot kullanılmıştır ancak "click" reaksiyonları pek çok açıdan bu yöntemlere kıyasla daha avantajlı konumdadır. Bu çalışmada, poliüretan sentezinde kullanılan diol bileşenleri farklı fonksiyonel gruplar bağlanarak çalışmanın maksadı doğrultusunda sentezlenmiştir. Sentezlenen bu diol bileşenleri üzerlerinde "click" reaksiyonlarında kullanılmaya uygun fonksiyonel gruplar taşımaktadır, bu gruplar listelenecek olursa alkin, antrasen ve perflorofenil ester gruplarıdır.

Yapılan ilk çalışmada PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) polimeri sentezlenmiş ve sırayla CuAAC, aktif ester sübstitüsyon reaksiyonu ve Diels-Alder

reaksiyonları kullanılarak poliüretan modifikasyonu gerçekleştirilmiştir. Yapılan deneylerde küçük organik moleküller kullanılmıştır. Deneylerden elde edilen sonuçlar doğrultusunda CuAAC, aktif ester sübstitüsyon reaksiyonu ve Diels-Alder reaksiyonları kullanılarak poliüretanların fonsiyonlandırılabileceği başarı ile gözlenmiştir.

Bu çalışmada yapılan ikinci aşamada ise PU-(Anthracene-*co*-Alkyne) sentezlenmiş ve kullanılacak "click" reaksiyonlarının verimlerinin belirlenmesi amacı ile küçük moleküllerle bir model reaksiyon gerçekleştirilmiştir. Model reaksiyonların başarı ile sonuçlanması sonrasında PU-(Anthracene-*co*-Alkyne) kopolimerinin iki farklı polimer ile graft edilmesi gerçekleştirilmiştir. Bu maksatla azit uç fonksiyonlu polietilen glikol ve malimid uç fonksiyonlu poli(metil metakrilat) sentezlenmiştir.

PU-(Anthracene-*co*-Alkyne) öncelikle azid uç fonksiyonlu polietilen glikol ile Cu (I) katalizörlüğünde oda sıcaklığında reaksiyona sokulmuş ve PU-*g*-PEG polimeri elde ediliştir. Bu aşamanın ardından PU-*g*-PEG ile malimid uç fonksiyonlu poli(metil metakrilat) kullanılarak 105°C'de Diels-Alder reaksiyonu gerçekleştirilmiş ve PU-*g*-(PEG, PMMA) sentezlenmiştir. Sentezlenen polimerler UV-, NMR ve GPC ölçümleri kontrol edilmiş ve yüksek verim ile düşük polidispersite indeksi ile başarı ile elde edilmiştir.

1. INTRODUCTION

Prof. Dr. Otto Bayer and coworkers discovered polyurethanes (PUs) in 1937 and the research on synthesis of PUs has gained a great importance since the World War II. The first PU is synthesized by the reaction between hexamethylene diisocyanate (HMDI) and hexane-1,6-diamine [1]. After the discovery a great research started on PUs and nowadays PUs are an important class of polymers for the field of academy and industry [2]. Polyurethanes are a very diverse group of polymers, which capable of exhibiting a wide range of properties by changing their molecular composition and topology, such as changing from smooth elastomeric membranes to rigid bulk structures. PUs can be prepared in different forms, e.g.; foam, fiber, film, tube, resin, and elastomer [3]. The most popular applications of PUs are in the field of medicine, insulation, automotive, coatings, paintings, electronics and adhesives [4].

In the preparation of PUs, the compound containing amino and carboxyl groups or organic halides and metal cyanides can be used [5]. On the other hand, synthesis of PUs via condensation polymerization between polyols and diisocyanates has still been the most versatile method [6]. While the most of PUs are thermoset, the thermoplastic PUs have found in a wide range of applications because the mechanical, thermal and chemical properties can be modified by the chemical nature of the polymer and composition of the starting materials [7].

In this work, attention has been paid to the functional diols since most of the commercially available diisocyanates do not contain suitable functionalities. Even though the functional diols are commercially available, these functional groups generally need to be protected during the polymerization to avoid side reactions by functional groups and should be removed after the polymerization to reactivate functional groups for modifications [6, 8]. Because of additional steps, protection and subsequent de-protection steps are inconvenient. Therefore, it is a great challenge to prepare functionalized diols, which will be used in the preparation of PU. Since these functional groups must be inert during the polymerization and allow efficient side chain modifications of PU after the polymerization [6, 8-10].

The click reactions which described by Sharpless and co-workers in 2001 [11], mostly fulfill these requirements for the synthesis of side chain functionalized PUs based on diols with clickable functional groups [6, 12-18]. These click reactions, copper catalyzed azide-alkyne cycloaddition (CuAAC) [19], thiol-ene [13-15], thiol-yne [20], nucleophilic substitution on perfluorophenyl ester [16], and Diels-Alder [17, 18] reactions have been recently employed for the synthesis of side chain-functional PUs.

In recent times, Du Prez group reported an efficient preparation of side chain functionalized linear PUs for the first time. Du Prez group accomplished that by reacting the one of two types of alkyne-functionalized diols, butandiol as chain extender and hexamethylene diisocyanate (HMDI) [19]. Subsequently, alkyne functionalized PU was clicked to a different azide functionalized compounds via CuAAC (catalyzed either by CuBr/ N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA) or $CuSO_4.5H_2O$/sodium ascorbate in dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO) at 50°C) and resulting material affords side chain-functionalized PUs having various degree of functionalization. Moreover, Du Prez group prepared PUs with clickable side chain groups, i.e. alkene, maleimide, and alkyne and allowed to react with thiols using the Michael thiol-ene [12], thiol-ene [14], and thiol-yne [20] reactions, respectively in order to quantitatively incorporate various functionalities.

However, the Diels-Alder reaction in PU chemistry is limited to a specific type of application which is based on exploitation of the thermally reversible nature of the Diels-Alder reaction between furan and maleimide [17, 18]. Wang group managed to produce a linear PU with Diels-Alder bonds and demonstrated the self-healing property of this PU under the heat treatment and the self-healing efficiency was determined up to 80% [17]. More recently, Du Prez group employed Diels-Alder reaction for the preparation of furan-based thermoset PUs having self-healing property [18]. In this regard, the diol with one furan functionality was first clicked with bismaleimide to yield a Diels-Alder adduct as a cross-linker and subsequently reacted with HMDI together with a poly(e-caprolactone) (PCL) diol in order to give final thermoset polyurethane in a one-pot reaction. The self-healing system operates in the cycles of retro-Diels-Alder and Diels-Alder at 100 and 40°C, respectively.

In addition, use of active esters are famous in the fields of peptide synthesis in organic chemistry, but also active ester reactions gains much interest in polymer chemistry.

Recently Hedrick and coworkers managed to produce PUs, which have pendant perfluorophenyl esters from perfluorophenyl ester-containing diol precursors [16]. Hedrick group have synthesized the functional PU by polyaddition reaction of functional diol and diisocyanate in the presence of triflic acid as catalyst and managed the postpolymerization with various primary amines efficiently.

The promising results from the previous works on the functionalized PUs enabled us to use CuAAC, Diels-Alder and active ester substitution reaction in combination for the preparation of graft PUs for the first time. In this work, we studied here a different application of Diels-Alder reaction, active ester substitution reaction and CuAAC in PU chemistry. We intended to incorporate linear polymer precursors to the PU backbone with the anthracene, alkyne and perfluorophenyl pendant units through Diels-Alder reaction, CuAAC and perfluorophenyl ester substitution reaction. The linear aliphatic PU with the anthracene, alkyne and perfluorophenyl ester pendant groups was first prepared and a model modification reaction with small molecules was studied, respectively by Diels-Alder reaction, CuAAC and perfluorophenyl ester substitution reaction (Figure 1.1). In the second work the linear aliphatic PU with the anthracene and alkyne pendant groups was first prepared and subsequently first azide terminated linear poly(ethylene glycol) (PEG) and second α-furan-protected-maleimide terminated poly(methyl methacrylate) (PMMA) precursors were introduced into this PU backbone to yield corresponding graft copolymers, PU-*g*-(PEG-PMMA) via Diels-Alder reaction and CuAAC as seen in Figure 1.2.

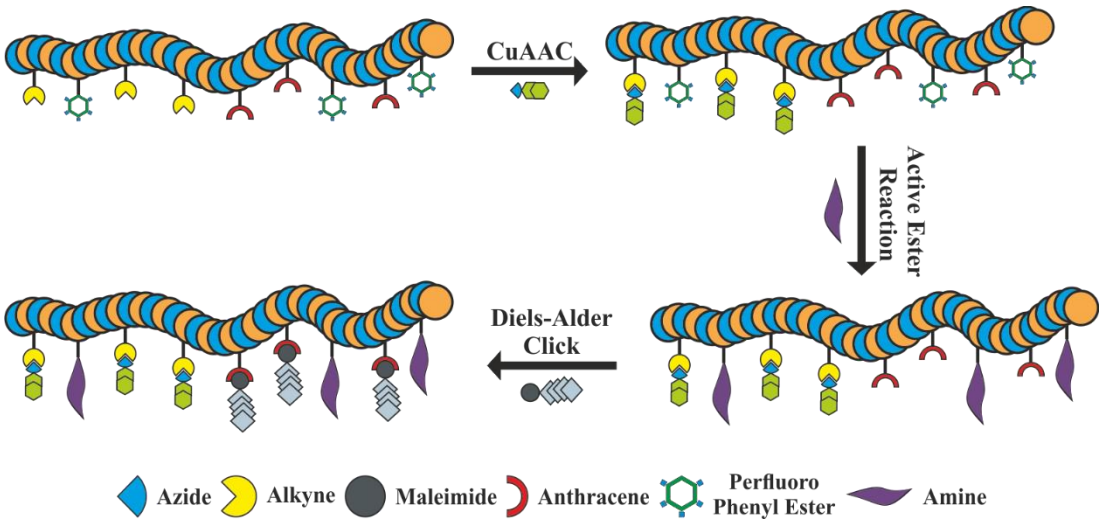


Figure 1.1 : Modification of PU-(Anthracene-co-Alkyne-co-Perfluorophenyl).

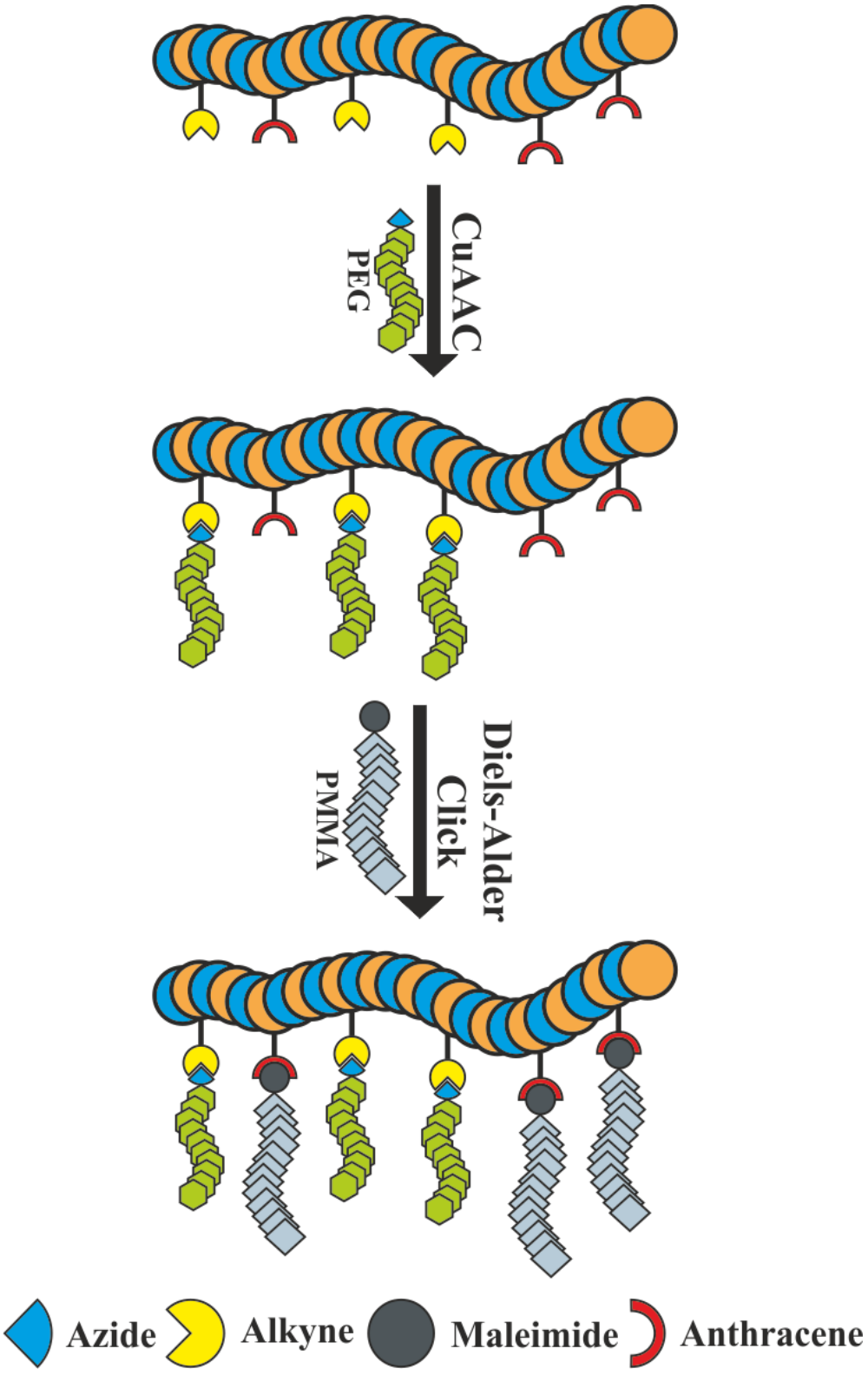


Figure 1.2 : Preparation of PU-*g*-(PEG-PMMA)

2. THEORETICAL PART

2.1 Living Polymerization

A well-defined polymer, with homogeneity in molecular weight, structure and composition, can only be synthesized by living ionic polymerizations or controlled/living radical polymerization (C/LRP) methods. Living polymerization was first clarified by Szwarc in 1955 as a chain growth process without chain breaking reactions such as transfer and termination reactions. Scwarc's pioneering work on the anionic polymerization of styrene, which initiated with sodium naphthalenide, opened the field of living polymers with controlling the molecular weight, molecular weight distributions and the structure of the end-groups [21].

After the discovery of living anionic polymerization, serious research on cationic polymerization was performed in the "living" era. The first system, which is used for initiation of such polymerization of vinyl ethers was an equimolar mixture of HI/I_2. In this system, iodine activates the initially formed adduct of HI to a vinyl ether. The fast initiation realized ideal living cationic polymerization of alkyl vinyl ethers. Thus, homopolymers and block copolymers with narrow molecular weight distributions were first synthesized by cationic polymerization [22].

Since then, much progress has been made in these living ionic polymerization techniques and polymerization of various monomers have been examined. For that manner numerous types of different initiators have been developed. While these techniques are undoubtedly successful, they do suffer from rigorous synthetic requirements. These requirements include the use of very pure reagents, the total exclusion of water and oxygen and incompatibility with a variety of functional monomers [23]. Definitely, with so many parameters to control, such requirements represent a grand challenge to synthetic polymer chemists and somewhat delay their practical use. Aware of the intrinsic limitations of ionic polymerizations, many efforts have been made to find new routes, which could address the development of a free radical polymerization. This process is tolerant to impurities, very versatile with

respect to compatibility with broad range of functional monomers, and relatively easy to implement in an industrial plant.

2.1.1 Controlled/"Living" Radical Polymerizations (C/LRP)

Conventional free radical polymerization (FRP), which provides high versatility, commercial productivity, and tolerance to many functionalities and impurities, remains the most convenient method to synthesize high molecular weights polymers. Moreover, free radical polymerization has been shown to be applicable to the polymerization of a wide range of monomers under mild reaction conditions over a large temperature range (-100 to 250°C) [24]. However, the major drawback of free radical polymerization is its poor-control in molecular weight and well-defined chain end structure. Also free radical polymerization is not capable to synthesize block copolymers and complex polymeric architectures.

Conventional free radical polymerization is a multistep polymerization technique and FRP consists of four elementary steps: initiation, propagation, termination, and chain-transfer reactions. The initiating radical is formed by various stimuli, e.g., thermolysis, photolysis, and redox processes. When the initiating radical formed, it reacts rapidly with vinyl monomers to grow the polymer chains. In contrast to ionic polymerizations, the radicals on the growing chains undergo bimolecular termination reactions by recombination or disproportionation, which gives dead polymers. On the other hand, the propagating radical also undergoes a chain-transfer reaction to generate a new propagating radical and a dead polymer chain. However, the resulting materials are polydisperse ($M_w/M_n>1.5$), because of slow initiation and fast radical-radical termination reactions. As a result of these reactions, the control over molecular weight and functionality is very difficult.

As a consequence of the ineffectiveness to accurately control molecular weight distribution and end functional groups, great progress has been made toward free radical polymerization achieving better control over polymer structure and possessing the characteristics of a living process. Thus, the concept of controlled/"living" radical polymerization (C/LRP) has been introduced, which consist of benefits of the prior methods; the control and precision of living polymerization and the robustness of radical polymerization [25-29]. C/LRP is a powerful process, which allows the preparation of polymers with well-defined features such as control over molecular

weights, narrow molecular weight distributions (M_w/M_n<1.1), high degrees of functionality and compositional variation under relatively mild conditions.

Even though FRP and C/LRP proceed via the same radical mechanism, the difference between FRP and C/LRP is that the radical end does not deactivate during the polymerization. Therefore, all of the C/LRPs based on the reversible generation of carbon-centered radicals. These carbon-centered radicals are called as dormant species, which possesses suitable functional groups at the polymer end for radical generation as seen in Figure 2.1. This "pseudo" deactivation of the growing radical species to the dormant species decreases the concentration of radical species in reaction intermediates. This reduction of radical concentration decreases the probability of undesirable side reactions and this "pseudo" deactivation makes the reaction proceed almost like a "living" process [30].

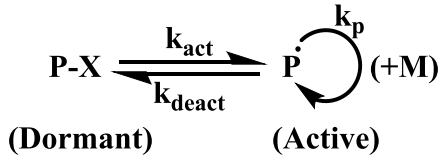


Figure 2.1 : Equilibrium between dormant and active species.

Consequently, the key to molecular weight control mainly connected to the predominant formation of the dormant species from the active radical species, as well as the establishment of an extremely fast activation-deactivation process relative to the fast propagation.

Although not truly ''living", "iniferter" system which is developed by Otsu in 1982 was the starting point for a C/LRP process [31]. Nowadays, among the most efficient C/LRP systems are nitroxide-mediated radical polymerization (NMP) [32, 33], atom transfer radical polymerization (ATRP) [23, 34-36], and reversible addition-fragmentation chain transfer (RAFT) [37, 38].

2.1.2 Atom transfer radical polymerization (ATRP)

Transition-metal mediated controlled/''living" radical polymerization reported independently by Matyjaszewski [39], Sawamoto [35] and Percec [40] in 1995. This polymerization techniques are one of the most powerful techniques to obtain polymers with high control over compositions, architectures, and functionalities. The polymerization, which is mechanistically similar to atom transfer radical addition

(ATRA), therefore, is often called as atom transfer radical polymerization (ATRP). ATRP is one of the most versatile methods of the controlled radical polymerization systems, which uses a wide variety of monomers, catalysts, solvents, and reaction temperature.

A general mechanism for ATRP is shown in Figure 2.2. ATRP is based on the reversible homolytic cleavage of the bond between carbon and halogen by a redox reaction. The propagating species $P_n^{\bullet}$ are generated through homolytic cleavage of the alkyl halogen bond (P_n-X) by a transition metal complex (activator, M_t^n-Y/Ligand, where Y can be another ligand or a counter ion). Two new species generate during on that redox reaction, one is an alkyl radical in the lower oxidation state ($P_n^{\bullet}$) and a transition metal complex (deactivator, X-M_t^{n+1}/Ligand) in the higher oxidation state. The formed radicals can initiate the polymerization by adding across the double bond of a vinyl monomer, propagate, terminate or become reversibly deactivated by the transition metal complex in the higher oxidation state to reform the dormant species and the activator. These reactions develop rapidly and the dynamic equilibrium between different species favors the dormant species.

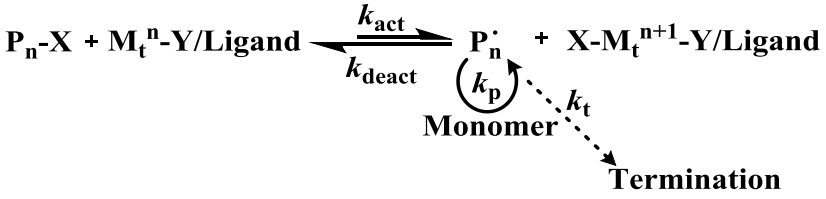


Figure 2.2 : A general mechanism for ATRP.

The process shown above occurs with a rate constant of activation (k_{act}) and deactivation (k_{deact}) respectively. Polymer chains propagate by the addition of the free radicals ($P_n^{\bullet}$) to monomers with the rate constant of propagation (k_p). Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. Other side reactions may additionally limit the achievable molecular weights and molecular weight distributions [41].

ATRP is a multicomponent system, it includes the monomer, an initiator with a transferable (pseudo) halogen and a catalyst (composed of a transition metal species

with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present in the reaction medium. Sometimes an additive is used. Basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents are discussed in the following section.

2.1.2.1 Basic components of ATRP

Monomers

Most of the vinyl monomers used in free radical polymerizations have also been successfully polymerized via ATRP, e.g. styrene derivatives, (meth)acrylates, (meth)acrylamides, dienes, and acrylonitrile which contain substituents that are capable of stabilizing the propagating radicals [42]. ATRP is tolerant to many functional polar groups on monomers, however, a few monomers can not be polymerized with currently available ATRP catalyst systems. Some functional groups react rapidly with the catalyst system (such as acids; (meth)acrylic acid) that creating metal carboxylates which are ineffective catalysts for ATRP. Some other monomers may be difficult to polymerize since they exhibit side reactions, such as 4-vinyl pyridine, which can undergo quaternization by the (alkyl halide) initiator [43]. For each monomer the rates of activation and deactivation (k_{act} and k_{deact}) are unique, and these constants define monomer's own equilibrium constant (K_{eq}) which determines the polymerization rate. The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides [23, 44].

Initiators

The main role of the initiator is to determine the concentration of dormant species and to provide end groups for polymer chains. Organic halides having a labile bond between carbon and halogen are the most successfully used initiators in ATRP. Generally, these organic halides contain electron withdrawing groups and/or atoms at α-carbon, such as carbonyl, aryl, cyano or halogens, to stabilize the generated free radicals.

The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide group (-X) should migrate rapidly and selectively between the growing chain and the transition metal complex.

When the halide group is chosen as fluorine, the bond between carbon and fluorine is not weak enough for the fast activation-deactivation cycle with atom transfer. Thus far, when halide groups is either bromine or chlorine, the molecular weight control is best. In addition, iodine works well for polymerization of acrylates in copper-mediated ATRP and has been found to lead controlled styrene polymerization in ruthenium-based ATRP [45, 46]. To obtain similar reactivity of the carbon-halogen bond in the initiator and the dormant polymer end, the structure of the alkyl group (-R) of the initiator should be similar to the structure of the dormant polymer end. Typical examples of that concern would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization [47], or 1-phenylethyl chloride for the initiation of a styrene polymerization [34].

The amount of initiator in the ATRP determines the final molecular weight of the resulting polymer at full monomer conversion. If initiation is fast and side reactions are negligible, the number of growing chain is constant and determined by initial initiator concentration. At living polymerization systems, the theoretical molecular weight or the degree of polymerization (DP) increases recioprocally with the initial concentration (equation **2.1**).

$$DP = \frac{[M_0]}{[Initiator_0]} xConversion \qquad \textbf{(2.1)}$$

The initiator can not only be a small molecule, but also a polyfunctional small molecule, or a macromolecule, which would produce end-functional polymers, star polymers, and graft copolymers, respectively.

Catalysts

Catalysts are the most important components of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. An efficient catalyst should be able to expand its coordination sphere and oxidation number upon halogen abstraction from an initiator (alkyl halide) or dormant polymer chains, and the metal center should have reasonable affinity toward a halogen to be able to abstract it. Additionally, the catalyst should not

participate in any side reactions, which would lower its activity or change the radical nature of the ATRP process.

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts, such as Re, Ru, Rh, Fe, Ni, Pd and Cu. Copper has been successfully used as catalysts for ATRP and it seems to be the most efficient metal as determined by the successful applications of its complexes as catalysts in the ATRP of a broad range of monomers in diverse media [42]. A recent work from Sawamoto and co-workers shows that the Rubased complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [48]. The transition metal complex is very often a metal halide, but pseudohalides, carboxylates, and compounds with noncoordinating triflate and hexafluorophosphate anions were also used successfully [49].

Ligands

Ligand plays a critical role in the activation/deactivation equilibrium in ATRP. The type of a ligand including electronic, steric characters and solubility, greatly affects the reactivity of the catalyst complex and control over the polymerization [34, 50]. The main role of a ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal, should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions.

Ligands for ATRP systems include multidentate alkyl amines, pyridines, pyridineimines, phosphines, ethers or half-metallocene species. Copper complexes with various multidentate nitrogen based ligands are most often used as ATRP catalysts such as PMDETA, and tris[2-(dimethylamino) ethyl]amine (Me_6-TREN) [51]. The ATRP catalytic activity of Cu(I) complexes increases in the order bipyridine (bpy) < 1, 1, 4, 7, 10, 10- hexamethyltriethylene tetramine (HMTETA) < PMDETA < tris(2-pyridylmethyl)amine (TPMA) < Me_6-TREN < dimethyl crossbridge cyclam (DMCBCy). The most active complex known to date is derived from the cross-bridged cyclam ligand DMCBCy (Figure 2.3) [23].

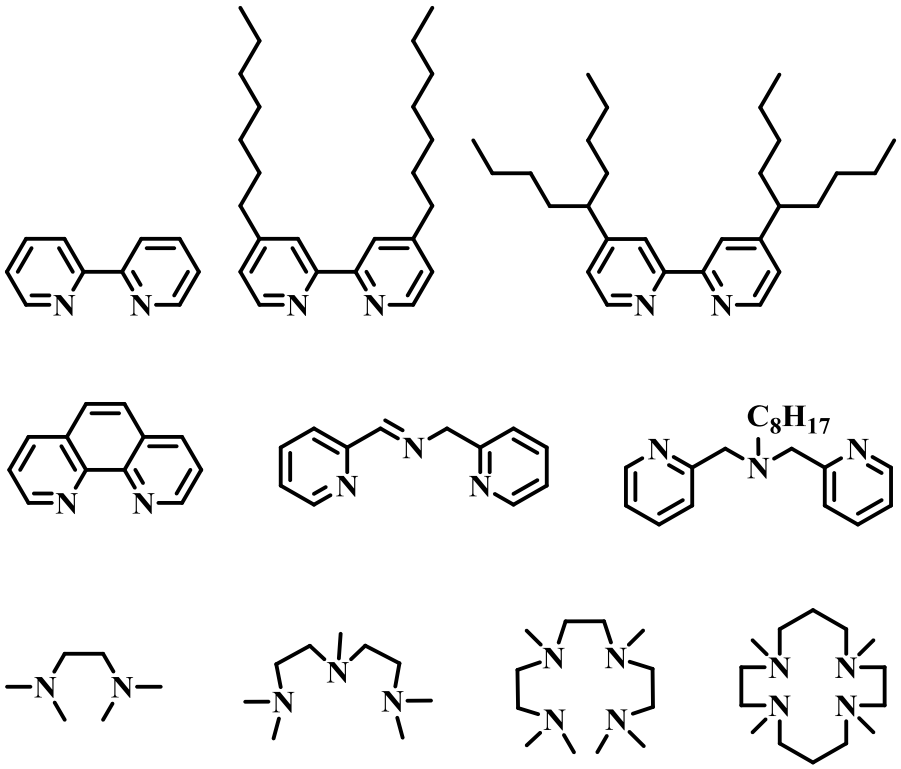


Figure 2.3 : The most common ligands for ATRP systems.

While nitrogen based ligands are typically used for copper-based ATRP, phosphorus-based ligands are used for most other transition metals in ATRP.

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Common solvents, including nonpolar (toluene, xylene, benzene), polar aprotic (diphenyl ether, dimetoxy benzene, anisole, N,Ndimethylformamide, ethylene carbonate, acetonitrile), and polar protic (alcohols, water), are employed for solubilizing the monomers, the produced polymers and the catalyst. A solvent also used to achieve the controlled polymerization condition. On the other hand, a solvent is sometimes necessary, especially when the polymer is insoluble in its monomer such as polyacrylonitrile. ATRP has also been successfully carried out under heterogeneous conditions (e.g., (mini)emulsion, suspension, or dispersion). Several factors affect the solvent choice for instance chain transfer to solvent and potential interactions between solvent and the catalytic. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [7] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent [52], should be minimized.

2.2 Polyurethanes

PUs were discovered in 1937 by Bayer and coworkers and the research on the synthesis of PUs has gained great importance since the World War II. The first PU is synthesized by the reaction between hexamethylene diisocyanate (HMDI) and hexane-1,6-diamine [1]. PUs are employed in a broad range of uses and applications, including machinery, transport, furnishing, textiles, papermaking, packaging, adhesives, sealants and medicine. Also the outstanding mechanical properties and biocompatibility of the polyurethanes makes them some of the most promising synthetic biomaterials [53].

Most of the polymers manufactured in industry possess a fairly simple chemical structure because the synthesis of these polymers consist one or two monomers therefore leading to the formation of homopolymers or copolymers. On the other hand, PUs comprise three monomers: a diisocyanate, a macroglycol (which is an oligomeric monomer) and a chain extender which possess more complex chemical structures [54].

Polyurethane copolymers built up by short, alternating polydisperse blocks of soft and hard segments. The soft segment is typically a low glass transition temperature (T_g) polyether, polyester or polyalkyldiol, generally of molecular weight 400-5000. The hard segment is usually a high glass transition temperature, possibly semicrystalline aromatic diisocyanate, linked with a low molecular weight chain extender. Because of the options available in selecting the chemistries and molecular weight of the various components and the ration in which they are reacted, that the PUs exhibit a broad range of physical properties [53]. By selecting the type of isocyanate and polyols, or combination of these groups, one can design the structure to obtain desired physical and chemical properties. The flexibility to design the structure during processing is one of the main advantages of PUs over other types of polymers. Urethane groups form strong hydrogen bonds among themselves and with different substrates. Strong intermolecular bonds make PUs useful for diverse applications in adhesives, coatings, elastomers and foams. One of the great advantages of polyurethanes arises from the high reactivity of isocyanates, which can react with a number of substances having different function al groups. This allows polymerization at relatively low temperatures and in short times (several minutes) [55].

2.2.1 Raw Materials of Polyurethanes

Polyurethanes are composed of three raw reactants: polyol, diisocynate and chain extender (diamine or diol). The final properties of the PUs are largely dependent on the chemical and physical nature of these three building blocks. Since the chemistry and functionality of the hydroxyl containing reactant (polyol) or the isocyanate can be varied, a wide range of linear, branched or cross-linked polymers with different properties can be obtained [54, 56, 57].

The properties of the PUs are due to the presence of urethane linkages in the molecular backbone (Figure 2.4). The type of diisocyanate, polyol and solvent used may affect the rate and the type of the reaction as well as the properties of the product.

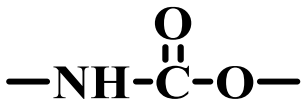


Figure 2.4 : Urethane linkage.

Polyols give high flexibility to the backbone of the network chains. Therefore, they are called soft domains or soft segments. Conversely, isocyanate and chain-extender components give rigidity to the chains and are called hard domains or hard segments (Figure 2.5) [57, 58].

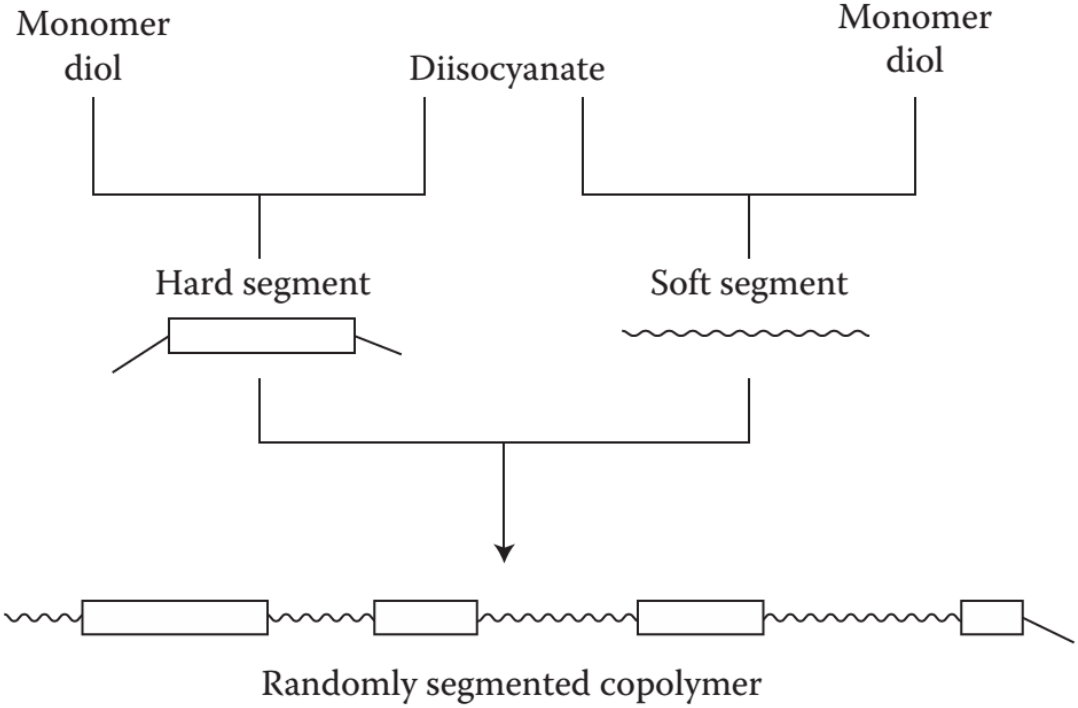


Figure 2.5 : Soft and hard segments of polyurethanes.

PUs are generally obtained by condensation reaction of diisocyanates and Polyols as shown in Figure 2.6.

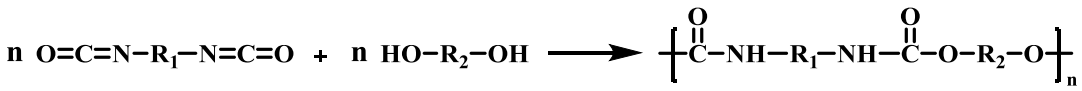


Figure 2.6 : Condensation reaction of diisocyanate and polyol.

In the preparation of polyurethanes, the compounds containing amino and carboxyl groups or organic halides and metal cyanides may also be used [5]. These reactions are summarized in Figure 2.7.

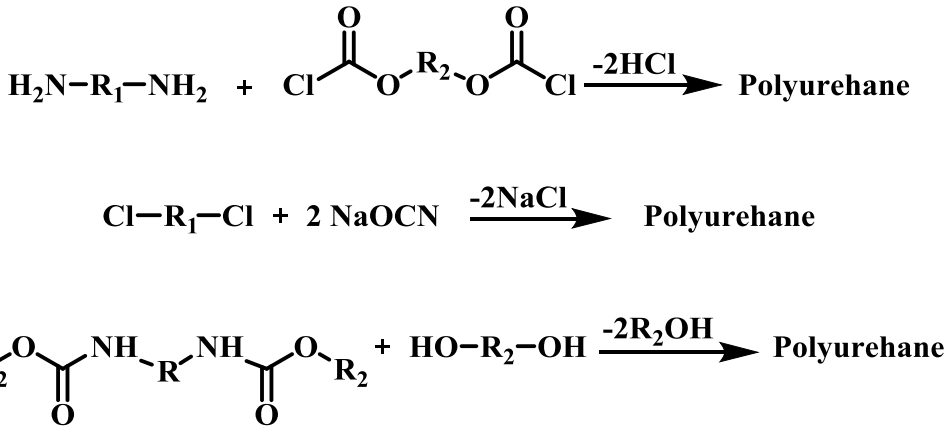


Figure 2.7 : Various reactions for polyurethane synthesis.

2.2.2 Isocyanates

Isocyanates are highly reactive chemicals and create several chemically different products when combined with hydroxyl and amine functional groups. Isocyanates with two or more -NCO groups in the molecule are required for the formation of polyurethanes. The high reactivity of isocyanate groups toward nucleophilic reagents is mainly due to the partially positive character of the carbon atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen. The electronegativity of the oxygen and nitrogen impart a large electrophilic character to the carbon in the isocyanate group. The high reactivity and polarizability of the double bonds permit multiple reactions, and because of this, isocyanates are widely used intermediate products [59].

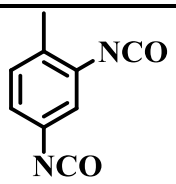
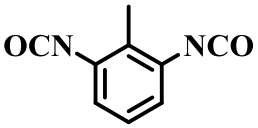
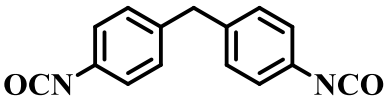
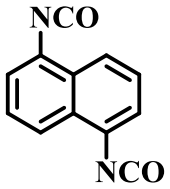
2.2.2.1 Types of isocyanates

Monoisocyanates are used as intermediates because of high reactive isocyanate group. On the other hand, multifunctional polyisocyanates is considerably more important than monoisocyanates, polyisocyanates give opportunity of building polymers. Diisocyanates contain two isocyanate groups and polyisocyanates contain two or more isocyanate groups. Common isocyanates used as building blocks for polyurethanes include aromatic and aliphatic isocyanates. However, aromatic polyisocyanates are commercially more available. On the other hand, aliphatic isocyanates are used also to fulfill desired properties of final product. The most common diisocyanates are toluene diisocyanate (TDI), methylene bis diphenylisocyanate (MDI), 1,5-naphthalene diisocyanate (NDI), hexamethylene diisocyanate (HDI) isophorone diisocyanate (IPDI) [57, 59, 60].

Aromatic Diisocyanates

Aromatic isocyanates are most widely used in the production of both flexible and rigid polyurethane foam coatings, adhesives, elastomers and fibers. Polyurethanes obtained from aromatic diisocyanates undergo slow oxidation rather than aliphatic ones, whereas polyether diols reduce thermal oxidative stability. Reactivity of isocyanates depends on their chemical structures and aromatic isocyanates are more reactive than aliphatic ones. The presence of electron withdrawing substituents on the isocyanate molecule increases the partial positive charge on the isocyanate carbon atom and moves the negative charge away from the site of reaction. This makes the transfer of the electron from the donor substance to the carbon easier, thus causing a faster reaction. On the other hand, the presence of electron-donating substituents on isocyanate compounds can cause slower reactions. Bulky groups in the ortho positions of aromatic isocyanates, and bulky and branched groups in the aliphatic isocyanates retard the reaction because of steric hindrance. In the reactions of diisocyanates, the reactivity of the second isocyanate decreases significantly after the first has been reacted [54, 61]. Commonly used aromatic isocyanates are listed in Table 2.1.

Table 2.1 : List of commonly used aromatic diisocyanates.

Name	Structure
Toluene 2,4-diisocyanate (TDI)	
Toluene 2,6-diisocyanate (TDI)	
4,4'-methylene diphenyl diisocyanate (MDI)	
p-phenylene diisocyanate (PDI)	
Naphthalene-1,5-diisoyanate (NDI)	

Toluene diisocyanate and 4,4′-methylene diphenyl diisocyanate are the most widely used isocyanates during the production of polyurethanes. TDI is a colorless liquid and it is usually used as a mixture of isomers. Boiling point of TDI is around 120°C at 10mmHg and the vapor pressure of TDI is $2.3x10^{-3}$ mmHg at 25°C. MDI is solid, which melts at 37°C, has a tendency to dimerize at room temperature. MDI has a lower vapor pressure (10^{-5} mmHg at 25°C) than TDI. MDI is generally used in elastomer and rigid foam production. Naphthalene-1,5-diisocyanate is commonly used in the production of high grade elastomers [4, 62].

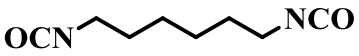
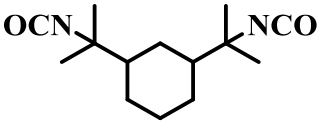
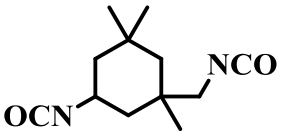
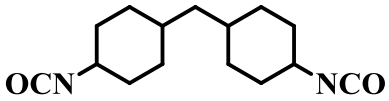
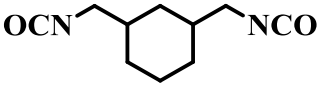
Aliphatic Diisocyanates

A disadvantage of aromatic diisocyanates is that they become yellow to dark brown when they are cured. Aliphatic diisocyanates are used in the production of color stable polyurethanes, although it is necessary to add antioxidants and UV-stabilizers to formulation to maintain the physical properties by time. Aliphatic isocyanates react in the rate order primary > secondary > tertiary, because of steric hindrance.

The least costly aliphatic diisocyanate is 1,6-hexamethylene diisocyanate (HDI), which is a colorless liquid and less reactive than both TDI and MDI. The use of HDI leads to urethane polymers with better resistance to discoloration, hydrolysis and heat degradation than TDI. HDI, m-tetramethylxylene diisocyanate (m-TMXDI) and

isophorone diisocyanate (IPDI) are used for aliphatic polyurethane synthesis. m-TMXDI and 4,4'-dicyclohexylmethane diisocyanate (Hydrogenated-MDI) are important in the production of non-discoloring polyurethanes, used in industry for surface coating [5, 57, 62, 63]. The most widely used aliphatic diisocyanates are listed in Table 2.2.

Table 2.2 : List of commonly used aliphatic diisocyanates.

Name	Structure
1,6-hexamethylene diisocyanate (HDI)	
m-tetramethylxylene diisocyanate (m-TMXDI)	
Isophorone diisocyanate (IPDI)	
4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI)	
1,4-cyclohexane diisocyanate (CHDI)	
Bis(isocyanatomethyl)cyclo-hexane (H_6XDI, DDI)	

2.2.2.2 Basic reactions of isocyanates

High reactivity of isocyanate group originates from its electronic structure as seen in resonance structures in Figure 2.8. Generally, electron-withdrawing group linked with R will increase the positive charge on carbon, so increasing the reactivity of the isocyanate group towards nucleophilic attack. On the other hand, electron-donating group will reduce the reactivity of isocyanate groups [64].

Figure 2.8 : Resonance structures of isocyanate group.

While nitrogen is less electronegative than oxygen, it follows that the highest electron density is on oxygen (electronegative) and the least on the carbon (electropositive). Thus, NCO easily reacts with proton donors as seen in Figure 2.9.

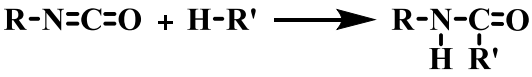


Figure 2.9 : Reaction between isocyanate group and proton donor.

Isocyanates are susceptible, however, to nucleophilic as well as electrophilic attacks. Typical nucleophilic reactions of isocyanates are urethane (carbamate) formation with alcohols and urea (carbamide) formation with amines (Figure 2.10). The reaction between isocyanate and hydroxyl groups like hydroxyl terminated polyesters and polyethers is the most important reaction to produce urethane [60].

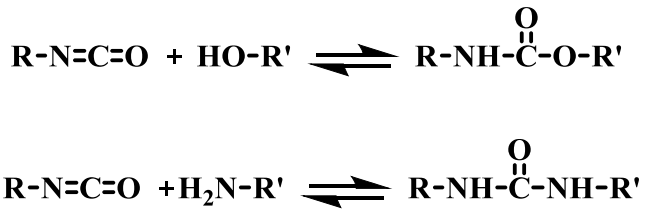


Figure 2.10 : Urethane and urea formation from isocyanates.

Aliphatic primary alcohols are most reactive than secondary and tertiary alcohols due to steric reasons, on the other hand phenol reacts with isocyanate more slowly than alcohols The reaction of isocyanate with alcohols is strongly exothermic (170–190 kJ/mol). One of the basic reactions in the urethane foam technology is the reaction of isocyanate with water; the initial product is carbamic acid, which is an unstable compound and further breaks down into carbon dioxide and primary amine. The amine will react immediately with another isocyanate to produce urea Figure 2.11 [55, 64].

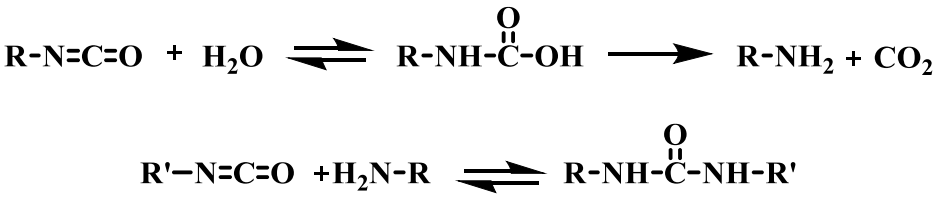


Figure 2.11 : The reaction between isocyanate and water.

Since the urethane group itself contains active hydrogen, also it could react with isocyanate to produce allophanate. This reaction proceeds to a significant degree at about 120–140°C but it could occur also at lower temperatures at high excess of isocyanates. The reaction of biuret formation from isocyanate and urea groups shows similar behaviors. Biuret formation reaction proceeds to a considerable measure above

100 °C. Both allophanate and biuret reactions are utilized to introduce crosslinks with the excess of isocyanate (Figure 2.12) [57, 65].

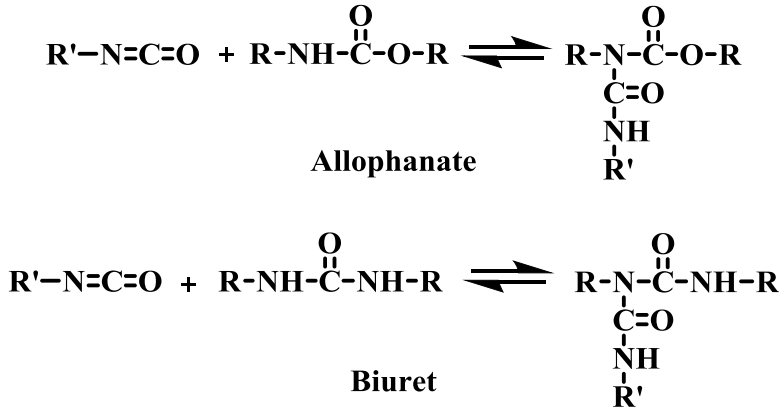


Figure 2.12 : Allophanate and biuret formation.

Furthermore, isocyanates react each other to form dimers (uretdiones) and trimmers (triisocyanurates). In dimer, formation isocyanates undergo exothermic cyclo-addition reaction resulting in a four membered ring. On the other hand, when three isocyanates reacts the resulting material is a six membered ring (Figure 2.13). Triisocyanurates possess exceptional thermal stability. The reaction, which generates trimmers, is used in industry to prepare thermally stable foams [64, 66].

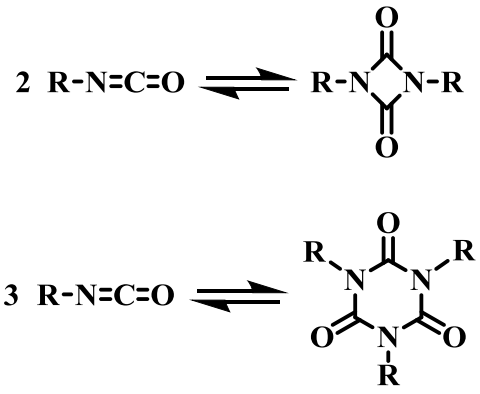


Figure 2.13 : Dimer and trimmer formations of isocyanates.

2.2.3 Polyols

Polyol compounds used in polyurethane production are generally compounds with molecular weights in the range of 400-5000Da. Depending on the chain length of these diols or glycol, the properties of the polyurethane change, such as if the polyol has a low molecular weight, the resulting polymer is a hard plastic, and if it has a high molecular weight, the resulting polymer is an elastomer. The reactivity of polyols are

not the same for all of the hydroxyl groups. Primary alcohols react readily at 25–50°C, while the secondary and tertiary alcohols are about 0.3 and 0.005 times less reactive than the primary ones, respectively. The most important polyols are hydroxyl functionalized polymers such as polyether, polyester, polyacrylate, polycarbonate, polycaprolactone and polyurethane polyols [67]. Polyester and polyether polyols are discussed on the next topics.

2.2.3.1 Polyester polyols

The polyester polyols are produced by the polycondensation of di- and polycarboxylic acids with an excess of polyfunctional alcohols. Building blocks for polyester polyols are presented in Table 2.3. The most important polycarboxylic acids and their anhydrides, which are available in industry, include aromatic acids (phthalic acid and isophthalic acid), aliphatic acids (adipic acid and maleic acid), cycloaliphatic acids (tetrahydrophthalic acid and hexahydrophthalic acid). Ethylene glycol, 1,2-propanediol, 1,6-hexanediol, neopentyl glycol, glycerol and trimethylolpropane, cycloaliphatic alcohols such as 1,4-cyclohexanedimethanol are aliphatic alcohols which are used as polyols.

Polyester polyols are synthesized by a polycondensation reaction of polycarboxylic acids with polyols, splitting of water. There are two ways to synthesize; the first one is azeotropic esterification performed in an azeotropic organic solvent. Azeotropic solvent acts as the carrier to remove the water from the reaction medium. The second one is melt condensation process in which the coreactants are reacted in melt at temperatures at approximately 160-260°C. The reaction can be performed either in vacuum or in a stream of inert gas to remove the water from the medium.

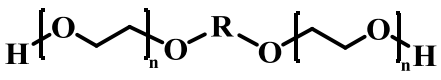
The polyester polyols are suitable for broad range applications from vehicle finishing to general industrial coatings. Commercial polyester products have a molecular weight of 500 to 5000 Da. They can whether be liquid or solid, hard and soft resins depending on the chemical structure (Table 2.3) [67, 68].

Table 2.3 : Building blocks for polyester polyols.

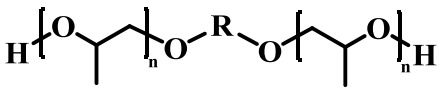
Diol/Triol	Dicarboxylic Acid
Ethylene glycol	Adipic acid
1,2-Propane diol	Maleic acid
1,4-Butane diol	Phthalic acid
1,6-Hexane diol	Hexahydrophthalic acid
Neopentyl glycol	Isophthalic acid
Diethylene glycol	
Glycerol	
Trimethylol propane	

2.2.3.2 Polyether polyols

Polyether polyols are produced by the addition of ethylene oxide and/or propylene oxide to a polyhydroxy molecule in the presence of a catalyst. Additionally, tetrahydrofuran is used commercially in the production of polyethers. Polyethers are mainly used for solvent-free formulations due to their low viscosity. Polyethers used in coatings applications and their molecular weight is between 500 and 2000 Da. The most commonly used polyols are polyethylene glycol (PEG) and polypropylene glycol (PPG) as seen in Figure 2.14. Group R comes from the starter diol such as ethylene glycol (R = - CH_2 - CH_2 -) [55, 59, 64].



PEG



PPG

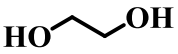
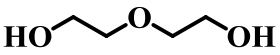
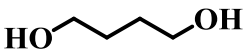
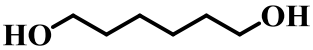
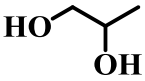
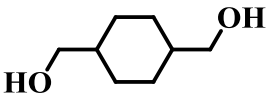
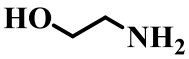
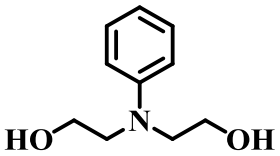
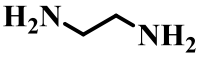
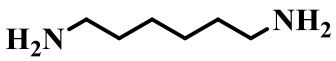
Figure 2.14 : Chemical structures of PPG and PPG.

2.2.4 Chain extenders and cross linkers

Cross-linking agents and chain extending agents are low molecular weight polyfunctional compounds and reactive with isocyanates and also known as curing agents. Generally, difunctional compounds are chain extenders and higher functional

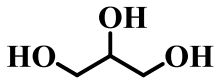
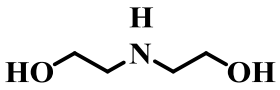
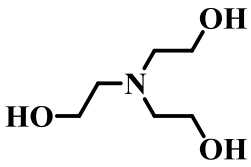
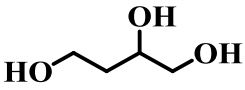
compounds are cross linkers. Chain extender can be difunctional glycols, diamines or hydroxyl compounds. That group comprises ethylene glycol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,2-ethylenediamine and 1,6-hexamethylene-diamine and typical chain extender agents are shown in Table 2.4.

Table 2.4 : Typical chain extenders.

Name	Structure
Ethylene glycol	
Diethylene glycol	
1,4-Butanediol	
1,6-Hexanediol	
1,2-Propanediol	
1,4-Cyclohexane dimethanol	
Ethanolamine	
N-Phenyldiethanolamine	
Ethylenediamine	
1,6-hexamethylenediamine	

Cross linkers have three or more functionality and they are used to increase the branching or cross-linking of polyurethane networks through the formation of urethane bonds. Typical cross linkers are glycerol, trimethylolpropane and amine compounds and shown in Table 2.5. Cross linker mostly used in rigid polyurethanes, coatings and adhesives [58, 69].

Table 2.5 : Typical cross linkers.

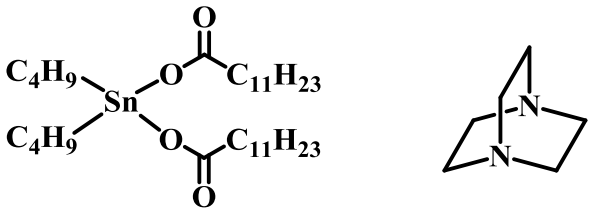
Name	Structure
Glycerol	
Diethanolamine	
Triethanolamine	
1,2,4-Butanetriol	

2.2.5 Catalyst

Catalysts are added to allow the reaction to take place at a rapid rate, and at lower temperatures. For the reaction of an isocyanate with an alcohol, many effective urethane catalysts are available. Most often used catalysts are tertiary amines, especially 1,4-diazabicyclo [2.2.2] octane (DABCO), triethyl amine (TEA), tetramethylbutane diamine (TMBDA) and organo tin compounds, especially dibutyltin dilaurate (DBTDL) and stannous octoate. In addition, phosphines, quaternary ammonium salts and phenols are used for acceleration different reactions of isocyanate [70].

In polyurethane coatings, aliphatic isocyanates are normally used with catalysts in order to compensate for their lower reactivity compared with aromatic isocyanates and thus satisfy the requirements for coating applications. There are two group catalysts are of key interest, which are metal catalysts and amine catalysts[66].

Metal catalysts activate the isocyanate group and accelerate the urethane reaction. A good example of metal catalyst is DBTDL and it is often used in polyurethane reactions. On the other hand amine catalysts, accelerate the urethane reaction primarily by activating the hydroxyl group. 1,4-diazobicyclo [2.2.2] octane is widely used in polyurethane reactions (Figure 2.15) [71].



DBTDL **DABCO**

Figure 2.15 : DBTDL and DABCO.

The catalytic effect of organometallic compounds is due to their complex forming ability with both isocyanate and hydroxyl groups. The mechanism proposed by Britain and Gemeinhardt is shown in Figure 2.16. The interation of metal cation with isocyanate, alcohol molecule results an intermediate complex in the first step, which may then readily rearrange to yield the urethane product [72-74].

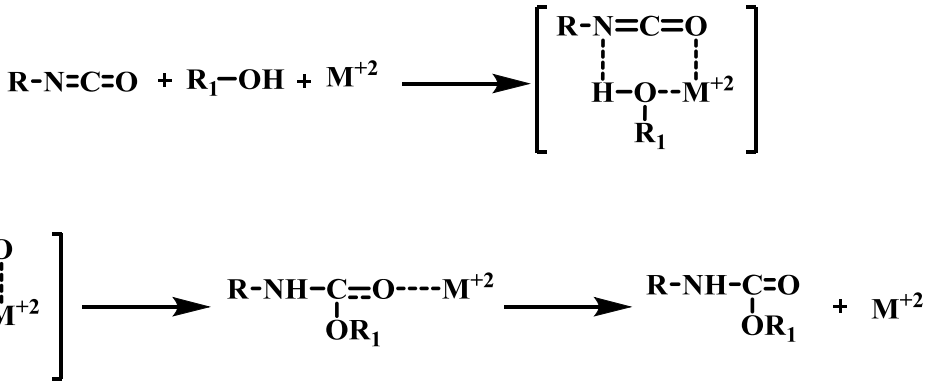


Figure 2.16 : Reaction mechanism of isocyanate and hydroxyl compound by organometallic catalysis.

Since different catalyst exhibit different catalytic activities, it is frequently used as combinations of different catalysts to get desired properties. Table 2.6 shows catalytic activities of different catalysts in a model isocyanate-hydroxyl reaction [55].

Table 2.6 : Relative activity of different catalysts in a model isocyanate-hydroxyl reaction.

Catalyst	Concentration, %	Relative activity
Uncatalyzed	0	1
TMBDA	0.1	56
DABCO	0.1	130
TMBDA	0.5	160
DBTDL	0.1	210
DABCO	0.3	330
Sn-octoate	0.1	540
DBTDL + DABCO	0.1 + 0.2	1000
Sn-octoate	0.3	3500
Sn-octoate + DABCO	0.3 + 0.3	4250

2.3 Click Chemistry

In 2001, Sharpless and coworkers introduced “click” chemistry, a new approach in organic synthesis that involves a collection of almost perfect chemical reactions. Sharpless describes click chemistry as tailored to generate substances quickly and reliably by joining small units together. Click chemistry can be summarized with only one sentence: Molecules that are easy to make. Sharpless also introduced some criteria in order to fulfill the requirements of click reactions, which reactions are modular, wide in scope, high yielding, create only inoffensive by-products, reactions are stereospecific, simple to perform and that require benign or easily removed solvent [11].

Nowadays there are several processes have been identified under this term in order to meet these criteria. Nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions fulfill Sharpless’s criteria (Figure 2.17) [75]. Among those selected reactions, copper (I)-catalyzed azide-alkyne (CuAAC), active ester reactions and Diels-Alder (DA) cycloaddition reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists. From this point of view, these reactions will shortly be summarized.

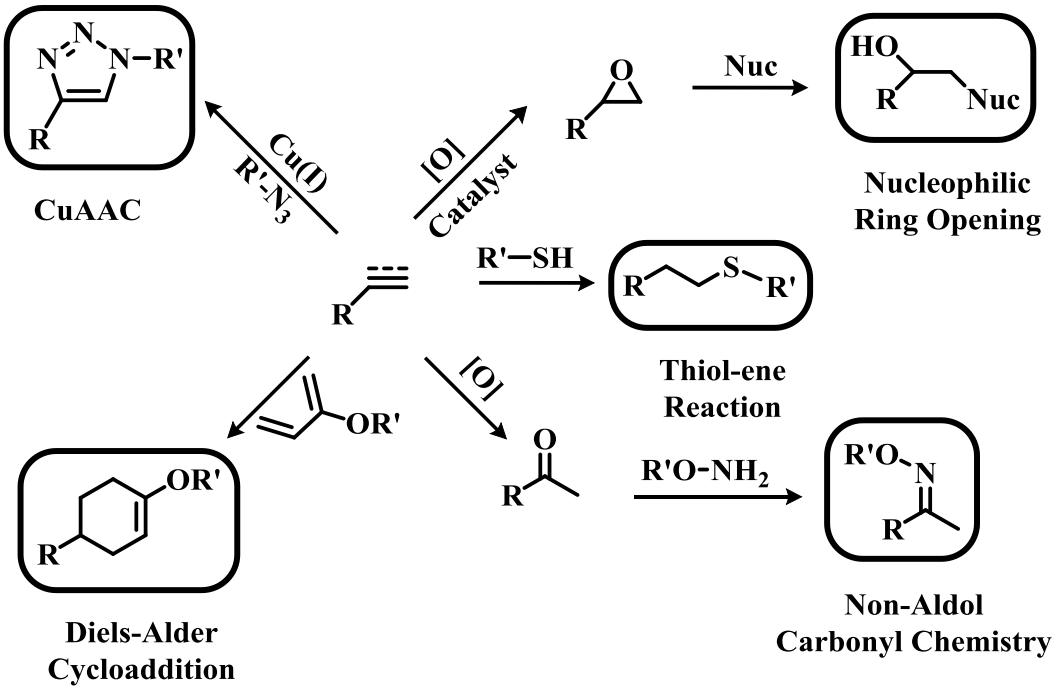


Figure 2.17 : General representation of popular click reactions.

2.3.1 Copper (I) catalyzed azide-alkyne cycloaddition (CuAAC)

The thermal reaction between organic azides and alkynes has been known for more than a century, the first 1,2,3-triazole being synthesized by A. Michael from phenyl azide and diethyl acetylenedicarboxylate in 1893. The reaction has been investigated in detail by Huisgen and coworkers in the middle of the 20th century in the course of their studies of the larger family of 1,3-dipolar cycloaddition reactions [76]. The Huisgen 1,3-dipolar cycloaddition reaction of alkynes and organic azides has gained considerable the most attention of any click reaction since 2001, CuAAC was realized independently by Fokin and Sharpless, and Meldal in 2002 [77, 78]. The conventional Huisgen cycloaddition of azides and alkynes is not appropriate the criterion of a click reaction, because of the high temperature necessity (>110 °C) and the lack of regiospecificity which produce products with a racemic mixture of 1,4-triazole and 1,5-triazole products as seen in Figure 2.18 [76]. The copper catalyzed reaction allows to proceed much faster under much milder conditions and produces only one isomer which is 1,4-regiosomer triazole [11, 79]. The great success of the Cu (I) catalyzed reaction is actually a virtually quantitative, very robust, insensitive, general, and orthogonal ligation reaction.

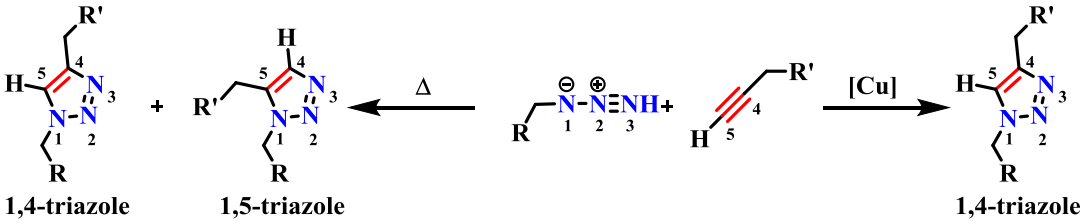


Figure 2.18 : Huisgen's 1,3-dipolar cycloaddition and CuAAC.

When the mechanism is catalyzed, Cu (I) can easily overcome the activation barrier as a result of this difference the CuAAC reaction rate is increased by a factor of 10^7 relative to the Huisgen 1,3-dipolar cycloaddition, so it considerably fast at and below room temperature [80, 81]. The reaction is not significantly affected by the steric and electronic properties of the functional groups attached to the azide and alkyne centers, and the CuAAC is fairly general with a broad range of alkynes and azides [82].

In fact, the discovery of Cu (I) as catalyst has a great importance which efficiently and regiospecifically combines terminal alkynes and azides under mild conditions. On the other hand, Fokin and Sharpless reported that only 1,5-disubstituted 1,2,3-triazole was obtained from terminal alkynes when the catalyst switched from Cu(I) to ruthenium(II) [83].

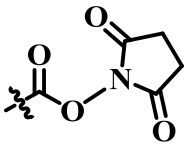
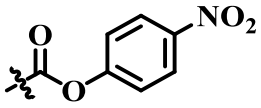
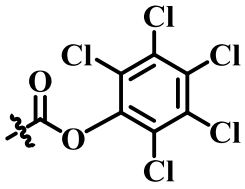
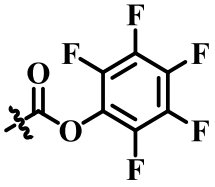
Although CuAAC reaction was initially postulated in general for organic synthesis, this strategy has also an enormous potential in polymer chemistry. The importance of CuAAC in polymer chemistry is the synthesis of functionalized polymers and the construction of polymers with well-defined architectures. Since the first report of click chemistry in polymer science which is published by Hawker, Sharpless and coworkers, the construction of well-defined and complex macromolecular architectures via click chemistry has been used in many study and the number of publications in this field has increased dramatically within the years [84].

2.3.2 Active esters

Active esters are famous in the field of peptide synthesis in organic chemistry [85]. This methodology has been much applied mainly to form peptide bonds under mild conditions in both liquid and solid phase synthesis. Many different active esters have been presented: thiophenylesters [86], activated methyl esters [87] and nitrothiophenyl esters [88]. New active esters were investigated after grooving interest, e.g.; *O*-acyl derivatives of hydroxylamines such as N-hydroxysuccinimide esters and many

different aryl esters with electron withdrawing substituents in the aromatic ring (Table 2.7). One of these esters, the pentachlorophenyl esters introduced by Kupryszewski which excel a high reactivity, but suffer from the steric effect of the bulky activating groups [89]. On the other hand, these esters have less potential to be used in solid phase peptide synthesis. A logical cure for this drawback was the replacement of the five chlorine atoms by fluorine. This change results a very powerful active ester with less steric hindrance that retains its reactivity even in the matrix used for solid phase peptide synthesis [90].

Table 2.7 : Common active esters.

Name	Structure
N-Hydroxysuccinimide ester	
4-nitrothiophenyl ester	
Pentachlorophenyl ester	
Pentaflorophenyl ester	

Functional polymers are usually prepared by polymerization of the desired functional monomers, however, the preparation of the corresponding monomers and/or their polymerization is often difficult or even impossible, especially when complex structures are desired. If prepolymers with reactive chemical functions in the side chain are utilized, in many cases these problems can be evaded; such as by protecting and de-protecting the functionality. As described above active esters are an ideal starting point in this kind of drawbacks. Because these reactive groups can be transformed into amide groups by polymer analogous reaction with primary or secondary amines in a quantitative and simple way, as shown in Figure 2.19 [91].

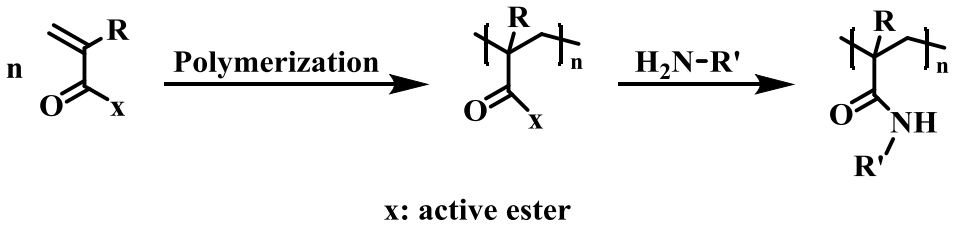


Figure 2.19 : Poly(active ester) as starting material.

Most examples of polymeric active esters that have been reported so far have focused on the modification of polymeric active esters either with primary amines or with peptides or metal binding ligands, which would have been difficult to introduce via direct polymerization [92]. As a result of, active ester polymers react fast and quantitatively with primary or secondary amines to form the corresponding poly(acrylamide) derivatives provides it allows an opportunity to obtain macromolecules with specialized functionalities [93]. The research for alternative active ester monomers and resulting polymers of these active ester monomers are still challenging. Pentafluorophenyl esters proved to be very effective in peptide chemistry and in polymer chemistry [16, 91].

2.3.3 Diels-Alder reaction

The Diels-Alder reaction (DA) is a concerned [4π+2π] cycloaddition reaction of a conjugated diene and a dienophile, 4 and 2 stand for the number of π electrons in the electronic rearrangement and the number of atoms of the unsaturated six-membered ring which is generated by the reaction of diene and dienophile. Reorganization of the π electrons, formation of two new sigma bonds and one new π bond all take place in a concerted manner as shown in Figure 2.20. Otto Diels and Kurt Alder discovered the Diels-Alder reaction in 1928, and the name of the reaction comes from their names; whom were awarded the Nobel Prize in 1950 [94, 95].

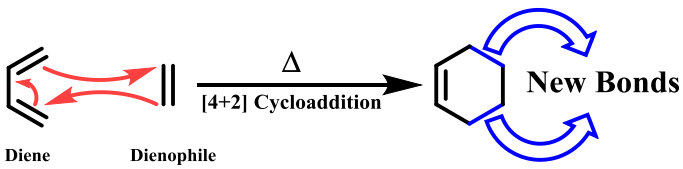


Figure 2.20 : General mechanism of Diels-Alder reaction.

Some attractive features of DA reactions are that they are thermally reversible. The decomposition of the cyclic product, which is called as retro-Diels-Alder, can be controlled by temperature (Figure 2.21) [96].

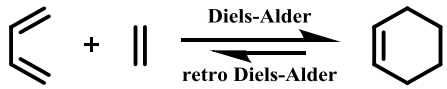


Figure 2.21 : General mechanism of DA and retro DA.

Conjugated dienes and dienophiles can be used in a great variety for constructing many different simple and complex molecules. In a typical Diels-Alder reaction the diene is substituted with electron donating functional groups such as -OR, -NR_2 and the dienophile is substituted with electron withdrawing functional groups such as –COOR, -CN, -CO, -NO_2 and in this cases the reactivity of diene and dienophile increases [97].

2.3.3.1 Stereochemistry of Diels-Alder reaction

There are stereo chemical and electronic requirements for the DA reaction to occur smoothly. Even if an s-trans conformation is more stable than an s-cis conformation, the diene must be in s-cis conformation instead of s-trans conformation to allow maximum overlap of the orbitals, which are participating in the reaction (s stands for single bond) (Figure 2.22). Over time s-trans conformer is converted to s-cis conformer when reaction proceeds.

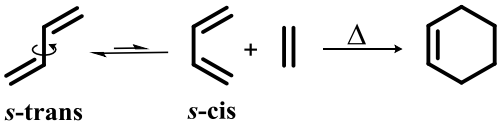


Figure 2.22 : Conformation to interconversion during DA reaction.

When diene is a cyclic compound, DA reaction produce bridged bicyclic compounds. There are two different configuration for the product is possible, endo and exo products. The dienophile can line up in two different ways. The substituent on the dienophile can point either toward the large bridge (endo) or away from the large bridge (exo) as seen in Figure 2.23 and Figure 2.24.

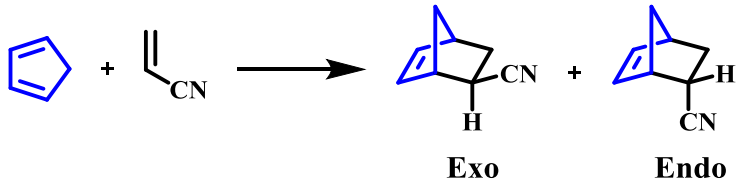
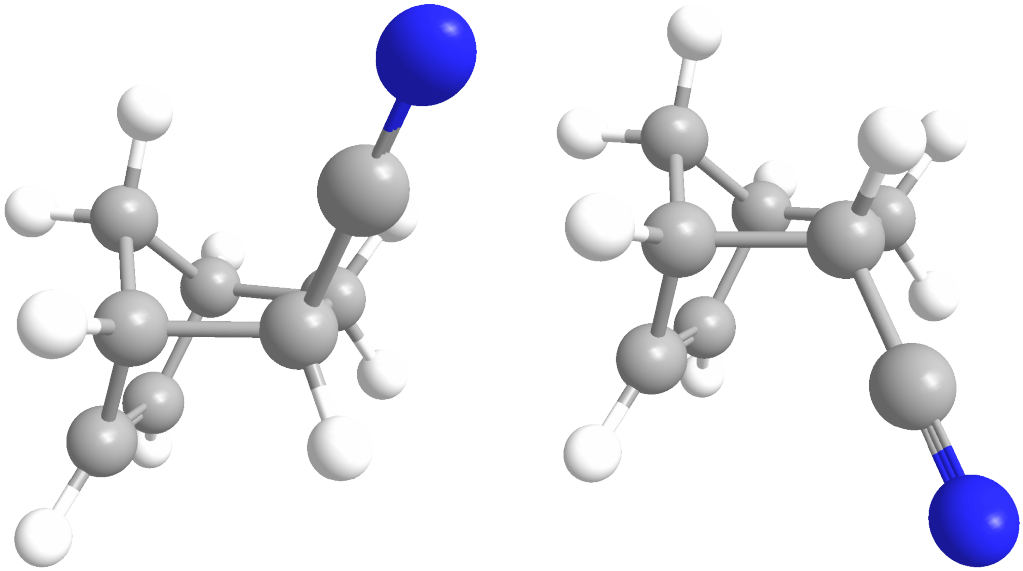


Figure 2.23 : Endo and exo products of DA reaction.



Exo Isomer Endo Isomer

Figure 2.24 : Stick-ball model of exo and endo products.

For instance, endo and exo products observed in most DA reactions, but the formation of endo product, which is more hindered product, puzzled the scientists. Woodward, Hoffmann, and Fukui used the molecular orbital theory to explain overlap of the p-orbitals on the substituents on the dienophile and with p-orbitals on the diene, which is favorable and helps to bring the two molecules together [98, 99]. Hoffmann and Fukui shared the 1981 Nobel Prize in chemistry for their molecular orbital explanation of DA reaction and other organic reactions. Figure 2.25 shows orbital overlaps of possible products, one easily can notice the favorable overlap of the diene and the substituent on the dienophile in the formation of the endo product.

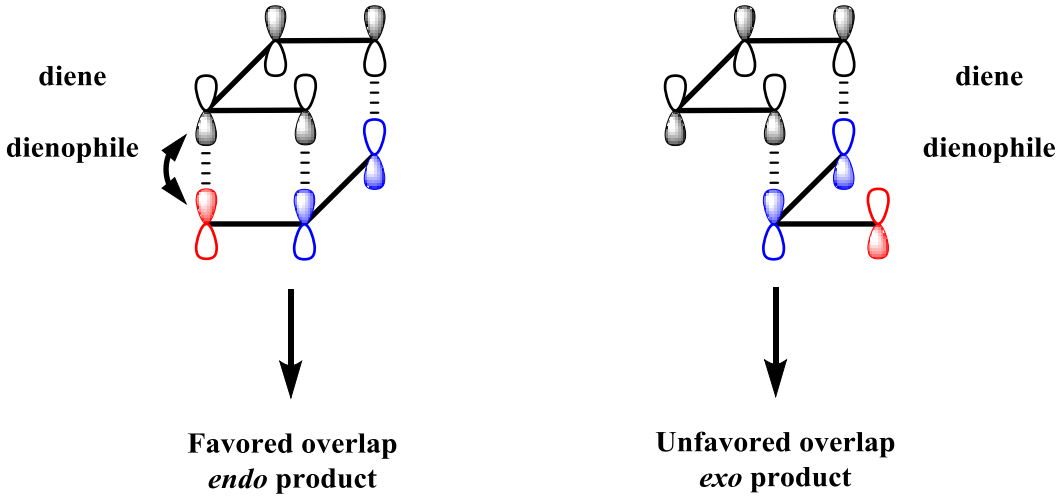


Figure 2.25 : Molecular orbitals overlaps of possible products of DA reaction.

DA reaction is a reversible reaction at elevated temperatures, because of this reason the endo/exo ratio depends on the reaction temperature. Therefore, use of high temperatures and extended reaction times can result in the formation of the exo product, which is thermodynamically more favorable, at the expense of the endo product, which is the kinetic product.

3. EXPERIMENTAL WORK

3.1 Materials

Methyl methacrylate (MMA, 99%, Aldrich) was passed through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum prior to use. Poly(ethylene glycol monomethyl ether) (PEG-OH) (M_n=550 g/mol, Acros) was dried over anhydrous toluene by azeotropic distillation. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled from benzophenone-Na. N,N-dimethylformamide (DMF, 99.8%, Aldrich) was dried and distilled under vacuum over CaH_2. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was dried and distilled over and P_2O_5. Diethyl ether (99.7%, Aldrich), 1.4-dioxane (99.8%, Aldrich), toluene (99.8%, Aldrich), methanol (99.8%, Aldrich) were used without further purification. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH before use. N,N'-Dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), CuCl (99.9 %, Aldrich), CuBr (99.9%, Aldrich), 9-anthracene methanol (97%, Aldrich), benzyl bromide (99.8%, Aldrich), octylamine (99%, Aldrich), propargyl alcohol (99%, Aldrich), pentafluorophenol (99%, Aldrich), sodium azide (99.5%, Aldrich), hexamethylenediisocyanate (HMDI, 98%, Aldrich), dibutyltindilaurate (DBTL, 95%, Aldrich) were used as received. All other reagents were purchased from Aldrich and used as received without further purification.

3.2 Instrumentation

^1H and ^{19}F NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using an Agilent VNMRS 500 (500 MHz) instrument. The conventional Gel Permeation Chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index, and UV detectors. Four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal

diameter, 300 mm length, packed with 5 μm particles) were used in series. The effective molecular weight ranges were 2000-4.000.000, 50-100.000, 500-30.000, and 500–20.000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at 30°C. Toluene was used as an internal standard. The molecular weights of the polymers were calculated on the basis of linear PS and PMMA standards (Polymer Laboratories). UV measurements were recorded using VWR UV-1600 PC spectrophotometer in CH_2Cl_2.

3.3 Synthetic Procedures

4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(1)** [100], 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(2)** [100], 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ester **(3)** [100], benzyl azide **(5)** [101], anthracen-9-yl methyl 3-hydroxy-2-(hydroxymethyl)-2-methyl propanoate **(10)** [102], propargyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate **(12)** [103] were prepared according to published procedures.

3.3.1 Synthesis of 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1)

Maleic anhydride (60.0 g, 0.6 mol) was suspended in 150 mL of toluene and the mixture warmed to 80 °C. Furan (66.8 mL, 0.9 mol) was added via syringe and the turbid solution was stirred for 8 h. The mixture was then cooled to ambient temperature white solids formed during standing were collected by filtration and washed with 2 × 30 mL of petroleum ether and once with diethyl ether (50 mL) afforded **1** as white needless. Yield: 80.2 g (80%). ^{1}H NMR ($CDCl_3$, δ) 6.57 (s, 2H, C*H*=C*H*, bridge protons), 5.45 (s, 2H, -C*H*O, bridge-head protons), 3.17 (s, 2H, C*H*-C*H*, bridge protons).

3.3.2 Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2)

1 (10.0 g, 60.0 mmol) was suspended in methanol (150 mL) and the mixture cooled to 0°C. A solution of ethanolamine (3.6 mL, 60 mmol) in 30 mL of methanol was added dropwise (10 min) to the reaction mixture, and the resulting solution was stirred for 5 min at 0°C, then 30 min at ambient temperature, and finally refluxed for 8 h. After

cooling the mixture to ambient temperature, solvent was removed under reduced pressure, and residue was dissolved in 150 mL of CH_2Cl_2 and washed with 3 × 100 mL of water. The organic layer was separated, dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave white-off solid, which was further purified by flash chromatography eluting with ethylacetate (EtOAc) to give the product as a white solid. Yield: 4.9 g (40%). ^{1}H NMR ($CDCl_3$, δ) 6.51 (s, 2H, C*H*=C*H*, bridge protons), 5.26 (s, 2H, -C*H*O, bridge-head protons), 3.74-3.68 (m, 4H, NC*H* 2 C*H* 2 O*H*), 2.88 (s, 2H, C*H*-C*H*, bridge protons).

3.3.3 Synthesis of 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo [5.2.1.0 2,6] dec-8-en-4-yl) ethyl ester (3)

In a 250 mL of round bottom flask were added **2** (2.0 g, 9.55 mmol) and Et_3N (1.44 mL, 10.54 mmol) in 100 mL of THF. The mixture was cooled to 0°C, and a solution of 2-bromo isobutyryl bromide (2.34 g, 10.0 mmol) in 25 mL of THF was added dropwise (30 min) to the reaction mixture. The white suspension was stirred for 3 h at 0°C and subsequently at ambient temperature for overnight. The ammonium salt was filtered off and the solvent was removed under reduced pressure to give a pale-yellow residue that was further purified by column chromatography over silica gel eluting with EtOAc/hexane (1/2) to give **3** as a white solid. (Yield=1.86 g, 55%). ^{1}H NMR ($CDCl_3$, δ) 6.49 (s, 2H, C*H*=C*H*, bridge protons), 5.24 (s, 2H, -C*H*O, bridge-head protons), 4.31 (t, *J*=5.2 Hz, 2H, NCH_2CH_2OC=O), 3.79 (t, *J*=5.2 Hz, 2H, NCH_2CH_2OC=O), 2.85 (s, 2H, C*H*-C*H*, bridge protons), 1.87 (s, 6H, C(CH_3)$_2$-Br).

3.3.4 Synthesis of furan protected maleimide end-functionalized PMMA (MI-PMMA) (4)

The MI-PMMA was prepared by ATRP of MMA. In a 50 mL of Schlenk tube, MMA (15 mL, 140 mmol), toluene (15 mL), PMDETA (0.293 mL, 1.4 mmol), CuCl (0.1388g, 1.4 mmol), and **3** (0.502g, 1.4 mmol) were added and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in argon. The tube was then placed in an oil bath thermostated at 40°C for predetermined times. The polymerization mixture was then diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in a vacuum oven at 40ºC. ($M_{n,GPC}$ = 2400 g/mol, $M_{n,NMR}$ = 2300 g/mol $M_{n,theo}$=1830 g/mol) ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, C*H*=C*H*, bridge protons), 5.3 (s,

2H, -C*H*O, bridge-head protons), 4.1 (m, 2H, NCH_2CH_2OC=O), 4.0-3.2 (br, OCH3 of PMMA and NCH2CH2OC=O), 2.9 (s, 2H, CH-CH, bridge protons), 2.5-0.5 (br, aliphatic protons of PMMA).

3.3.5 Synthesis of benzyl azide (5)

To a stirred solution of the benzyl bromide (0.4276 g, 2.5 mmol) in a 50 mL water/acetone mixture (1:4) was added NaN_3 (0.244 g, 3.75 mmol).The resulting suspension was stirred at 60°C for 24 hours. DCM was added to the mixture and the organic layer was separated. The aqueous layer was extracted with 3 x 10 mL aliquots of DCM and the combined organic layers were dried over Na_2SO_4. Solvent was removed under reduced pressure and **5** afforded as colorless oil (Yield=0.3 g, 90%). 1H NMR ($CDCl_3$, δ) 7.32-7.43 (m, 5H, aromatic protons), 4.35 (s, 2H CH_2-N_3).

3.3.6 Synthesis of tosylated PEG (6)

Me-PEG-OH (M_n=550 g/mol) (5 g, 9.09 mmol) was dissolved in 150 mL of CH_2Cl_2 and TEA (12.66 mL, 90 mmol) was added to this solution. The mixture was cooled to 0°C and toluene-4-sulfonyl chloride (tosyl chloride) (8.66 g, 45 mmol) in CH_2Cl_2 were added dropwise (30 min) to the reaction mixture. Than the reaction mixture was stirred overnight at room temperature. First, it was extracted with cold 4 M HCl, then with distilled water and dried over Na_2SO_4. The organic phase was evaporated and white solid was further purified by column chromatography over silica gel eluting with firstly CH_2Cl_2 and secondly with MeOH/ CH_2Cl_2 (1/6) to give **6** as colorless viscous liquid. (Yield=5.8 g, 91 %). ^{1}H NMR ($CDCl_3$, δ) 7.80 and 7.34 (8H, PEG-$OSO_2C_6H_4CH_3$), 4.15 (2H, OCH_2CH_2-$OSO_2C_6H_4CH_3$), 3.63 (OCH_2CH_2 repeating unit of PEG), 3.37 (3H, CH_3-PEG$OSO_2C_6H_4CH_3$) 2.44 (3H, PEG-$OSO_2C_6H_4CH_3$).

3.3.7 Synthesis of azide end functional PEG (PEG-azide) (7)

Tosylated-PEG, **6** (5.8 g, 8.24 mmol) was dissolved in DMF (20 mL) and sodium azide (NaN_3) (5.36 g, 82.3 mmol) was added to this solution. After stirring the reaction mixture overnight at room temperature, CH_2Cl_2 and water were added and the organic layer was extracted three times with water and dried over Na_2SO_4. Solvent was removed under reduced pressure and **7** afforded as colorless viscous liquid (Yield=4.51 g, 95 %). ^{1}H NMR ($CDCl_3$, δ) 3.63 (m, OCH_2CH_2 repeating unit of PEG), 3.36 (5H, CH_3-PEG-N_3 and CH_2O-N_3).

3.3.8 Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (8)

The 2,2-bis(hydroxymethyl)propionic acid (16.0 g, 119.2 mmol) along with p-TSA (0.9 g, 4.64 mmol), and 2,2-dimethoxypropane (22.4 mL, 178.8 mmol) dissolved in 80 mL of dry acetone, and stirred 2h at room temperature. In the vicinity of 2h, while stirring continued the reaction mixture was neutralized with 12 mL of totally NH_4OH (25%), and absolute ethanol (1:5), filtered off by-products and subsequent dilution with dichloromethane (240 mL), and once extracted with distilled water (80 mL). The organic phase dried with Na_2SO_4 concentrated to white solid after evaporation of the solvent (Yield=14.8 g 71%). ^{1}H NMR ($CDCl_3$, δ) .4.17 (d, 2H, CC*H*$_2$O), 3.67 (d, 2H, CC*H*$_2$O), 1.45 (s, 3H, C*CH*$_3$), 1.42 (s, 3H, C*CH*$_3$), 1.21 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.9 Synthesis of anthracen-9-ylmethyl 2,2,5-trimethyl-1,3-dioxane-5 carboxylate (9)

9-Anthracene methanol (5 g, 24 mmol) was dissolved in 100 mL of CH_2Cl_2 and **8** (5.01 g, 28:8 mmol), and DMAP (0.88 g, 7.2 mmol) were added to the reaction mixture in that order. After stirring 5 minutes at room temperature, DCC (5.94 g, 28.8 mmol) dissolved in 20 mL of CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. Then reaction mixture was extracted with water/CH_2Cl_2 (1:4) two times and combined organic phase was dried with Na_2SO_4. Solvent was evaporated and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (9:1) to give pale yellow solid (Yield=5.32 g; 60.8 %). ^{1}H NMR ($CDCl_3$, δ) 8.51 (s, 1H, Ar*H* of anthracene), 8.33 (d, *J*=8.9 Hz, 2H, Ar*H* of anthracene), 8.04 (d, *J*=7.9 Hz, 2H, Ar*H* of anthracene), 7.60-7.47 (m, 4H, Ar*H* of anthracene), 6.2 (s, 2H, C*H*$_2$-anthracene), 4.15 (d, *J*=11.8 Hz, 2H, CCH_2O), 3.59 (d, *J*=11.8, 2H, CCH_2O), 1.39 (s, 3H, CCH_3), 1.37 (s, 3H, CCH_3), 1.10 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.10 Synthesis of anthracen-9-yl methyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (anthracene diol) (10)

Anthracen-9-ylmethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate, **9** (5.32 g, 14.6 mmol) was dissolved in a mixture of 50 mL of THF and 50 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. The precipitated product was filtered off and reaction mixture was concentrated and extracted with 160 mL of

CH_2Cl_2 and 40 mL of water. The combined organic phase was dried with Na_2SO_4. Solvent was evaporated under reduced pressure to give anthracene diol as pale yellow solid (Yield=4.41 g, 93 %). ^{1}H NMR ($CDCl_3$, δ) 8.53 (s, 1H, Ar*H* of anthracene), 8.32 (d, *J*=8.9 Hz, 2H, Ar*H* of anthracene), 8.05 (d, J=8.5 Hz, 2H, Ar*H* of anthracene), 7.61-7.56 (m, 2H, Ar*H* of anthracene), 7.53-7.48 (m, 2H, Ar*H* of anthracene),6.22 (s, 2H, C*H*$_2$-anthracene), 3.86 (dd, *J*=11.2, 6.3 Hz, 2H, C*H*$_2$OH), 3.68 (dd, *J*=11.3, 5.9 Hz, 2H, C*H*$_2$OH), 0.98 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.11 Synthesis of prop-2-yn-1-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (11)

Propargyl alcohol (1.394 mL, 23.9 mmol) was dissolved in 100 mL of CH_2Cl_2 and **8** (5 g, 28.7 mmol), and DMAP (0.585 g, 4.79 mmol) was added to the reaction mixture in that order. After stirring 5 min at room temperature, DCC (5.93 g, 28.7 mmol) dissolved in 20 mL of $CH_2Cl_2$was added. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. Then reaction mixture was extracted with water/CH_2Cl_2 (1:4) two times, and combined organic phases were dried with Na_2SO_4. Solvent was evaporated and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (9:1) to give pale yellow viscous liquid (Yield=3.8 g; 75%). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J*=2.5 Hz, 2H, CH≡CC*H*$_2$O), 4.18 (d, *J*=11.9 Hz, 2H, CC*H*$_2$O), 3.64 (d, *J*=11.9 Hz, 2H, CC*H*$_2$O), 2.46 (t, *J*=2.5 Hz, 1H, C*H*≡CCH_2O), 1.41 (s, 3H, CC*H*$_3$) 1.37 (s, 3H, CC*H*$_3$), 1.19 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.12 Synthesis of prop-2-yn-1-yl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (alkyne diol) (12)

Prop-2-yn-1-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate, **11** (3.8 g, 17.9 mmol) was dissolved in a mixture of 40 mL of THF and 40 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. The precipitated product was filtered off and reaction mixture was concentrated and extracted with 160 mL of CH_2Cl_2 and 40 mL of water. The combined organic phase was dried with Na_2SO_4. Solvent was evaporated under reduced pressure to give propargyl diol as colorless viscous liquid (Yield=2.95 g, 96%). ^{1}H NMR ($CDCl_3$, δ) 4.73 (d, *J*=2.5 Hz, 2H, CH≡CC*H*$_2$O), 3.87 (d, *J*=11.3 Hz, 2H, C*H*$_2$OH), 3.70 (d, *J*=11.3 Hz, 2H, C*H*$_2$OH), 2.49 (t, *J*=2.5 Hz, 1H, C*H*≡CCH_2O), 1.09 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.13 Synthesis of perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (13)

2,3,4,5,6-pentafluorophenol (3 g, 16.3 mmol) was dissolved in 100 mL of CH_2Cl_2 and **8** (3.4 g, 19.6 mmol), and DMAP (0.398 g, 3.26 mmol) was added to the reaction mixture in that order. After stirring 5 min at room temperature, DCC (4.04 g, 19.6 mmol) dissolved in 20 mL of $CH_2Cl_2$was added. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. Then reaction mixture was extracted with water/CH_2Cl_2 (1:4) two times, and combined organic phases were dried with Na_2SO_4. Solvent was evaporated and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (9:1) to give white solide (Yield=4.58 g; 83%). ^{1}H NMR ($CDCl_3$, δ) 4.32 (d, *J*=11.9 Hz, 2H, CC*H*$_2$O), 3.79 (d, *J*=11.8 Hz, 2H, CC*H*$_2$O), 1.48 (s, 3H, CC*H*$_3$) 1.43 (s, 3H, CC*H*$_3$), 1.34 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$). ^{19}F NMR ($CDCl_3$, δ) -152.95 (d, *J*=17.6 Hz, 2F, o-*F*), -157.81 (t, *J*=21.7 Hz, 1F, p-*F*), -162.32 (t, *J*=20.0 Hz, 2F, m-*F*).

3.3.14 Synthesis of perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (perfluorophenyl diol) (14)

Perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate, **11** (4.58 g, 13.5 mmol) was dissolved in a mixture of 40 mL of THF and 40 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. The precipitated product was filtered off and reaction mixture was concentrated and extracted with 160 mL of CH_2Cl_2 and 40 mL of water. The combined organic phase was dried with Na_2SO_4. Solvent was evaporated under reduced pressure to give perfluorophenyl diol white solid (Yield=3.96 g, 98%). ^{1}H NMR ($CDCl_3$, δ) 4.07 (d, *J*=11.0 Hz, 2H, C*H*$_2$OH), 3.88 (d, *J*=10.9 Hz, 2H, C*H*$_2$OH), 1.31 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$). ^{19}F NMR ($CDCl_3$, δ) -152.74 (d, *J*=17.3 Hz, 2F, o-*F*), -157.47 (t, *J*=21.6 Hz, 1F, p-*F*), -162.09 (t, *J*=21.7 Hz, 2F, m-*F*).

3.3.15 General procedure for the preparation of pendant anthracene and alkyne functional polyurethane (PU-(anthracene-*co*-alkyne)) (15)

10, anthracene diol (0.5 g, 1.54 mmol), **12,** alkyne diol (0.265 g, 1.54 mmol), HMDI (0.495 mL, 3.08 mmol), and DBTDL (0.091 mL, 0.154 mmol) were dissolved in CH_2Cl_2 (10 mL). Subsequently, the solution was bubbled with nitrogen for 30 min and

stirred at room temperature for 10 days. After that time, the polymer solution was precipitated in 50 mL of methanol and the solvent was removed by decantation. The residual solid was dissolved in THF and consequently precipitated in methanol. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=1.1 g, 86%, $M_{n,GPC}$=11088 g/mol, M_w/M_n=1.28, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.47 (s, Ar*H* of anthracene), 8.31 (s, Ar*H* of anthracene), 8.00 (s, Ar*H* of anthracene), 7.59–7.42 (m, Ar*H* of anthracene), 6.16 (s, CH_2-anthracene), 5.13-4.88 (br, N*H* of PU), 4.69 (s, CH≡CCH_2O), 4.29–4.02 (m, CH_2OC=O of PU), 3.75–3.54 (m, CH_2OH and CH_2N=C=O end group protons of PU), 3.17–2.89 (m, CH_2NHC=O of PU), 2.47 (s, C*H*≡CCH$_2$O), 1.52–1.00 (m, CCH_3 and (CH_2)$_4$ of PU).

3.3.16 General procedure for the preparation of pendant anthracene, perfluorophenyl and alkyne functional polyurethane (PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl)) (16)

10, anthracene diol (0.75 g, 2.31 mmol), **12,** alkyne diol (0.299 g, 1.73 mmol), **14,** perfluorophenyl diol (0.52 g, 1.73 mmol) HMDI (0.929 mL, 5.78 mmol), and DBTDL (0.171 mL, 0.289 mmol) were dissolved in CH_2Cl_2 (10 mL). Subsequently, the solution was bubbled with nitrogen for 30 min and stirred at room temperature for 10 days. After that time, the polymer solution was precipitated in 50 mL of methanol and the solvent was removed by decantation. The residual solid was dissolved in THF and consequently precipitated in methanol. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=1.687 g, 66%, $M_{n,\,GPC}$=15600 g/mol, M_w/M_n=1.37, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.48 (s, Ar*H* of anthracene), 8.31 (s, Ar*H* of anthracene), 8.00 (s, Ar*H* of anthracene), 7.59–7.43 (m, Ar*H* of anthracene), 6.16 (s, CH_2-anthracene), 5.18-4.86 (br, N*H* of PU), 4.68 (s, CH≡CCH_2O), 4.43–4.03 (m, CH_2OC=O of PU), 3.79–3.54 (m, CH_2OH and CH_2N=C=O end group protons of PU), 3.20–2.90 (m, CH_2NHC=O of PU), 2.47 (s, C*H*≡CCH$_2$O), 1.52–1.00 (m, CCH_3 and (CH_2)$_4$ of PU). ^{19}F NMR ($CDCl_3$, δ) -152.74 - -153.24 (br, o-*F*), -156.95 - -157.51 (br, p-*F*), -161.78 - -162.28 (br, m-*F*).

3.3.17 Copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction of PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) and benzyl azide (17)

PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl), **16** (0.3 g, 0.677 mmol of alkyne), benzyl azide, **5** (0.1692 mL, 1.354 mmol), PMDETA (0.071 mL, 0.338 mmol), CuBr

(0.0486 g, 0.338 mmol) and DMF (5 mL) were added to a 10 mL of Schlenk tube. Reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After the specified time, solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in methanol and solvent was removed by decantation. The dissolution-precipitation procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40°C for 24 h (Yield=0.22 g, 68%, $M_{n,\ GPC}$=15360 g/mol, M_w/M_n=1.15, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.47 (s, Ar*H* of anthracene), 8.30 (s, Ar*H* of anthracene), 8.00 (s, Ar*H* of anthracene), 7.60 – 7.42 (m, Ar*H* of anthracene and C=C*H*N of triazole), 7.37 – 7.19 (m, Ar*H* of benzyl), 6.15 (s, CH_2-anthracene), 5.49 (s, CH=CCH_2O), 5.19 (s, Ph-CH_2), 4.85 – 4.49 (br, N*H* of PU), 4.38 – 4.00 (m, CH_2OC=O of PU), 3.17 – 2.88 (m, CH_2NHC=O of PU), 1.50 – 1.00 (m, CCH_3 and (CH_2)$_4$ of PU). ^{19}F NMR ($CDCl_3$, δ) -152.75 – -153.19 (br, o-*F*), -156.97 – -157.51 (br, p-*F*), -161.72 – -162.24 (br, m-*F*).

3.3.18 Perfluorophenyl ester substitution reaction of 17 and octylamine (18)

Pendant perfluorophenyl functional PU **(17)** (0.11 g, 0.229 mmol of perfluorophenyl ester), octylamine (0.0766 mL, 0.458 mmol) and TEA (0.0638 mL, 0.458 mmol) was dissolved in 10 mL of THF. Subsequently, the solution was bubbled with nitrogen for 10 min and stirred at room temperature for 24 h. After that time, the polymer solution was concentrated and precipitated in 50 mL of methanol and the solvent was removed by decantation. The residual solid was dissolved in THF and consequently precipitated in methanol. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=0.062 g, 58%, $M_{n,\ GPC}$=16320 g/mol, Mw/Mn=1.17, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.47 (s, Ar*H* of anthracene), 8.30 (s, Ar*H* of anthracene), 8.00 (s, Ar*H* of anthracene), 7.61 – 7.42 (m, Ar*H* of anthracene and C=C*H*N of triazole), 7.37 – 7.20 (m, Ar*H* of benzyl), 6.15 (s, CH_2-anthracene), 5.48 (s, OCH_2-triazole), 5.19 (s, Ph-CH_2), 4.90 – 4.52 (br, N*H* of PU), 4.35 – 4.02 (m, CH_2OC=O of PU), 3.24 – 2.87 (m, CH_2NHC=O of PU and NHCH_2 of octylamine), 1.48 – 1.00 (m, CCH_3 of PU, (CH_2)$_4$ of PU and NH(CH_2)$_6$CH$_3$), 0.90 – 0.80 (m, NH(CH$_2$)$_6$CH_3).

3.3.19 Diels-Alder reaction of 18 and 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.02,6]dec-8-ene-3,5-dione (19)

Pendant anthracene functional PU, **18** (0.062 g, 0.133 mmol of anthracene) and **2** (0.0557 g, 0.266 mmol) were dissolved in 30 mL of dioxane/toluene mixture (2:1, vol/vol). After that, the solution was bubbled with nitrogen for 10 min and refluxed at 105°C in the dark for 48 h. The solvent was evaporated and the residual solid was dissolved in THF and subsequently precipitated in 50 mL of methanol and solvent was removed by decantation. This dissolution–precipitation procedure was repeated two times and the obtained product was dried in vacuum oven at 40°C for 24 h (Yield=0.045 g, 62%, $M_{n,GPC}$=17630 g/mol, M_w/M_n 1.22, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.58 (s, C=C*H*N of triazole), 7.48 – 7.10 (m, aromatic protons), 5.57 – 5.10 (m, CH_2-bicyclic, OCH_2-triazole, Ph-CH_2 and N*H* of PU), 4.77 (s, C*H* bridge-head proton), 4.36 – 4.05 (m, CH_2OC=O of PU), 3.38 – 2.90 (m, CH_2NHC=O of PU, C*H*–C*H* bridge protons, OCH_2CH$_2$N, OCH$_2$CH_2N, NHCH_2 of octylamine and NCH$_2$CH$_2$O*H*), 1.51 – 1.10 (m, CCH_3 of PU, (CH_2)$_4$ of PU and NH(CH_2)$_6$CH$_3$), 0.90 – 0.83 (m, NH(CH$_2$)$_6$CH_3).

3.3.20 CuAAC reaction of PU-(anthracene-*co*-alkyne) and benzyl azide (20)

PU-(anthracene-*co*-alkyne), **15** (0.2 g, 0.466 mmol of alkyne), benzyl azide, **5** (0.116 mL, 0.931 mmol), PMDETA (0.049 mL, 0.233 mmol), CuBr (0.0334g, 0.233 mmol) and DMF (5 mL) were added to a 10 mL of Schlenk tube. Reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After the specified time, solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in methanol and solvent was removed by decantation. The dissolution-precipitation procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40°C for 24 h (Yield=0.121 g, 46%, $M_{n,\ GPC}$=14380 g/mol, M_w/M_n=1.32, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.46 (s, Ar*H* of anthracene), 8.30 (s, Ar*H* of anthracene), 7.99 (s, Ar*H* of anthracene), 7.59 – 7.42 (m, Ar*H* of anthracene and C=C*H*N of triazole), 7.37 – 7.18 (m, Ar*H* of benzyl), 6.15 (s, CH_2-anthracene), 5.48 (s, CH=CCH_2O), 5.19 (s, Ph-CH_2), 4.78 – 4.48 (br, N*H* of PU), 4.24 – 4.00 (m, CH_2OC=O of PU), 3.77 – 3.56 (m, CH_2OH and CH_2N=C=O end group protons of PU), 3.13 – 2.87 (m, CH_2NHC=O of PU), 1.48 – 0.98 (m, CCH_3 and (CH_2)$_4$ of PU).

3.3.21 Diels-Alder reaction of 20 and 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.02,6]dec-8-ene-3,5-dione (21)

Pendant anthracene functional PU, **20** (0.100 g, 0.206 mmol of anthracene) and **2** (0.086 g, 0.413 mmol) were dissolved in 30 mL of dioxane/toluene mixture (2:1, vol/vol). After that, the solution was bubbled with nitrogen for 10 min and refluxed at 105°C in the dark for 48 h. The solvent was evaporated and the residual solid was dissolved in THF, and subsequently precipitated in 50 mL of methanol. This dissolution–precipitation procedure was repeated two times and the obtained product was dried in vacuum oven at 40°C for 24 h (Yield=0.08 g, 64%, $M_{n,\,GPC}$=16970 g/mol, M_w/M_n=1.25, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.58 (s, C=C*H*N of triazole), 7.48 – 7.10 (m, aromatic protons), 5.57 – 5.10 (m, CH_2-bicyclic, OCH_2-triazole, Ph-CH_2 and N*H* of PU), 4.77 (s, C*H* bridge-head proton), 4.36 – 4.05 (m, CH_2OC=O of PU), 3.38 – 2.90 (m, CH_2NHC=O of PU, C*H*–C*H* bridge protons, OCH_2CH$_2$N OCH$_2$CH_2N, NHCH_2 of octylamine and NCH$_2$CH$_2$O*H*), 1.51 – 1.10 (m, CCH_3 of PU, (CH_2)$_4$ of PU and NH(CH_2)$_6$CH$_3$), 0.90 – 0.83 (m, NH(CH$_2$)$_6$CH_3).

3.3.22 CuAAC reaction of PU-(anthracene-*co*-alkyne) and azide end functional PEG (22)

PU-(anthracene-*co*-alkyne), **15** (0.25 g, 0.582 mmol of alkyne), PEG-azide, **7** (0.502 g, 0.873 mmol), PMDETA (0.0608 mL, 0.291 mmol), CuBr (0.0418g, 0.291 mmol) and DMF (5 mL) were added to a 10 mL of Schlenk tube. Reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After the specified time, solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in diethyl ether and solvent was removed by decantation. The dissolution-precipitation procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40°C for 24 h (Yield=0.16 g, 41%, $M_{n,\,GPC}$=9200 g/mol, M_w/M_n=1.21, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.48 (s, Ar*H* of anthracene), 8.32 (s, Ar*H* of anthracene), 8.00 (s, Ar*H* of anthracene), 7.79 (s, C=C*H*N of triazole), 7.58 – 7.42 (m, Ar*H* of anthracene), 6.16 (s, CH_2-anthracene), 5.23 (s, CH=CCH_2O), 4.51 (s, NCH_2CH$_2$O of PEG), 4.23 – 4.01 (m, CH_2OC=O of PU), 3.85 (s, NCH$_2$CH_2O of PEG),3.78 – 3.46 (m, CH_2OH and CH_2N=C=O end group protons of PU and OCH_2CH_2 of PEG), 3.37 (s, OCH_3 end-

group of PEG), 3.15 – 2.90 (m, C*H*$_2$NHC=O of PU), 1.50 – 1.01 (m, CC*H*$_3$ and (C*H*$_2$)$_4$ of PU).

3.3.23 Diels-Alder reaction of 22 and furan protected maleimide end-functionalized PMMA (MI-PMMA) (23)

Pendant anthracene functional PU, **22** (0.16 g, 0.239 mmol of anthracene) and MI-PMMA **4** (0.862 g, 0.359 mmol) were dissolved in 30 mL of dioxane/toluene mixture (2:1, vol/vol). After that, the solution was bubbled with nitrogen for 10 min and refluxed at 105°C in the dark for 48 h. The solvent was evaporated and the residual solid was dissolved in THF, and subsequently precipitated in 50 mL of methanol/diethyl ether mixture (1:1, vol/vol). This dissolution–precipitation procedure was repeated two times and the obtained product was dried in vacuum oven at 40°C for 24 h (Yield=0.3 g, 58%, $M_{n,\ GPC}$=8380 g/mol, M_w/M_n=1.47, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.79 (s, C=C*H*N of triazole), 7.41 – 7.10 (m, aromatic protons), 5.22 (br, C*H*$_2$-bicyclic), 5.31 – 4.80 (s, OC*H*$_2$-triazole and N*H* of PU), 4.76 (s, C*H* bridge-head proton), 4.52 (s, NC*H*$_2$CH$_2$O of PEG), 4.34 – 4.07 (m, C*H*$_2$OC=O of PU), 3.86 (s, NCH$_2$C*H*$_2$O of PEG), 3.78 – 3.20 (br, C*H*–C*H* bridge protons, OC*H*$_2$CH$_2$N, OCH$_2$C*H*$_2$N, OC*H*$_3$ of PMMA, OC*H*$_3$ end-group of PEG C*H*$_2$OH and C*H*$_2$N=C=O end group protons of PU), 3.09 (s, C*H*$_2$NHC=O of PU).

4. RESULTS AND DISCUSSION

Click reactions, as coined by Sharpless [11], are highly efficient and specific reactions have emerged as a powerful tool for polymer chemists. Click chemistry have been extensively employed for preparation of well define polymers and post-polymerization functionalization of a wide variety of polymer backbones [104-106].

Previous works on modification of polyurethanes via click reactions have opened the way through highly tunable polyurethanes. In fact, many different reactions have been used for polyurethane modifications. DA reaction [107], CuAAC [19] and active ester compounds such as pentafluorophenyl ester [16] have been employed for that manner. Therefore, we have combined three different click reactions, DA reaction, CuAAC and active ester substitution reaction. In that purpose two different polyurethanes synthesized with three functional diols, first polyurethane prepared by copolymerization of anthracene and alkyne functional diols and second PU prepared by copolymerization of anthracene, alkyne and pentafluorophenyl ester functional diols. To verify the efficiency of DA reaction, CuAAC and active ester substitution reaction for both of the polymers model reactions conducted via small functional molecules. After the verification of efficiency PU-*g*-(PEG, PMMA) synthesized by corresponding reactions.

4.1 Preparation of ATRP Initiator and DA Reactants for Model Reactions

The ATRP initiator with proper functionality for DA reaction were synthesized within three steps. First, maleic anhydride and furan were reacted in toluene at reflux temperature for 8 h to give 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(1)** as seen in Figure 4.1. The anhydride **1** was obtained as small white needless.

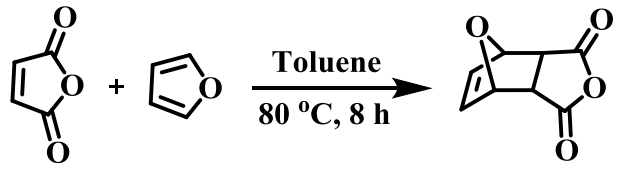


Figure 4.1 : Synthesis of 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(1)**.

The reaction of the anhydride **1** was then carried out to give the 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(2)**. In this reaction, the anhydride **1** was suspended in MeOH and a solution of ethanolamine in MeOH was added dropwise at 0°C, then resulting mixture refluxed for 8 h (Figure 4.2). Finally, compound **2** was obtained as a white solid.

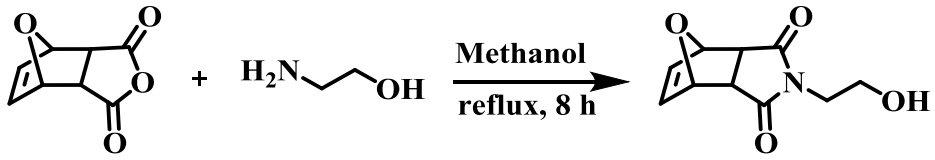


Figure 4.2 : Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(2).**

The synthesis of 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo [5.2.1.02,6] dec-8-en-4-yl) ethyl ester **(3)** was obtained via an esterification reaction between **2** and 2-bromoisobutryl bromide in THF at room temperature (Figure 4.3). **2** and Et_3N was dissolved in THF and cooled to 0°C, and a solution of 2-bromoisobutyryl bromide THF was added dropwise to the reaction mixture and subsequently stirred at room temperature for overnight. Finally, compound **3** obtained as white solid.

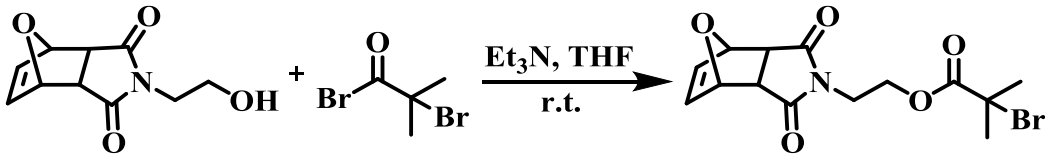


Figure 4.3 : Synthesis of 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo [5.2.1.0 2,6] dec-8-en-4-yl) ethyl ester **(3).**

From overlay ^1H NMR spectra (Figure 4.4) of **3**, it was clearly seen that the methyl protons next to Br were detected at 1.87 ppm and the methylene protons next to the ester unit at 4.31 ppm. Moreover, the characteristic protons of the adduct were also detected at 6.49 ppm (bridge vinyl protons), 5.24 ppm (bridgehead protons) and 2.85

ppm (bridge protons) respectively. These results confirmed that the synthesis of **3** was achieved.

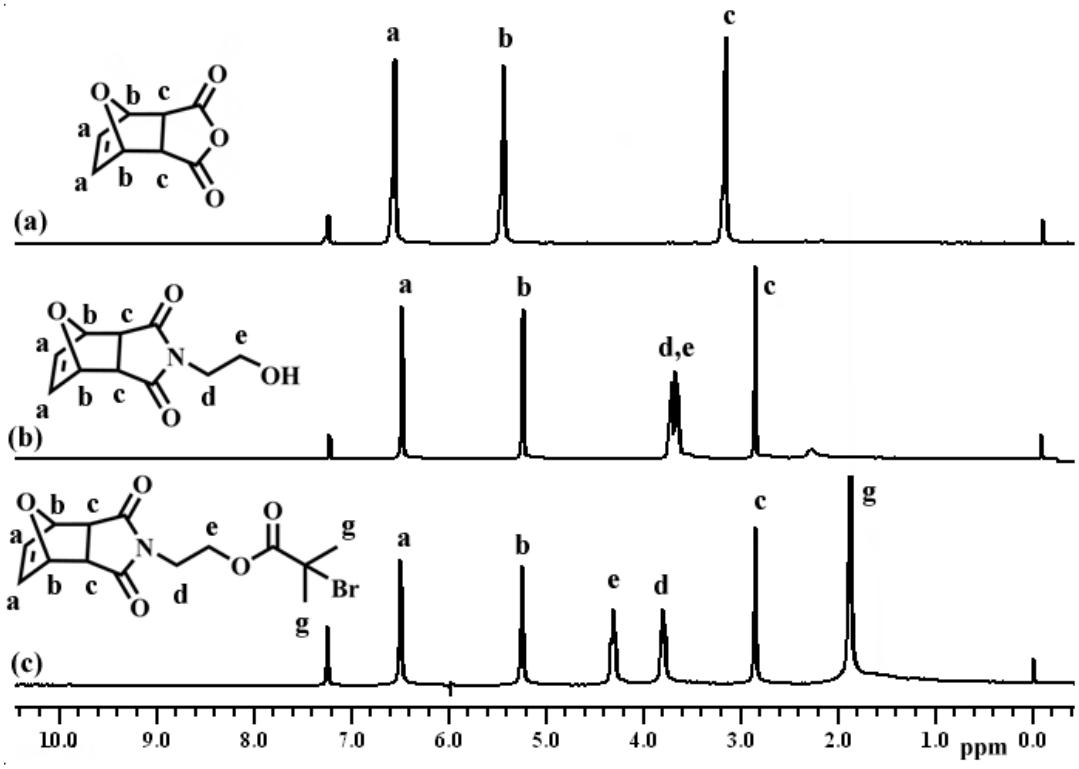


Figure 4.4 : ^{1}H NMR spectra of: **a)** 4,10-dioxatricyclo [5.2.1.02,6] dec-8-ene-3,5-dione **(1)**; **b)** 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.02,6] dec-8-ene-3,5-dione **(2)**; **c)** 2-bromo-2- methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo [5.2.1.02,6] dec-8-en-4-yl) ethyl ester **(3)**, in $CDCl_3$.

4.2 Preparation of MI-PMMA

Furan protected maleimide end-functionalized PMMA (MI-PMMA) **(4)** was obtained by ATRP of MMA. Since furan protection was easily de-protected at elevated temperatures, the polymerization temperature for MMA were purposely kept low in order to prevent possible copolymerization of maleimide and monomers during polymerization. Then compound **3** was used as an initiator in ATRP of MMA in the presence of CuCl/PMDETA, which used as catalyst system at 40°C to obtain MI-PMMA as one of the graft chains (Figure 4.5).

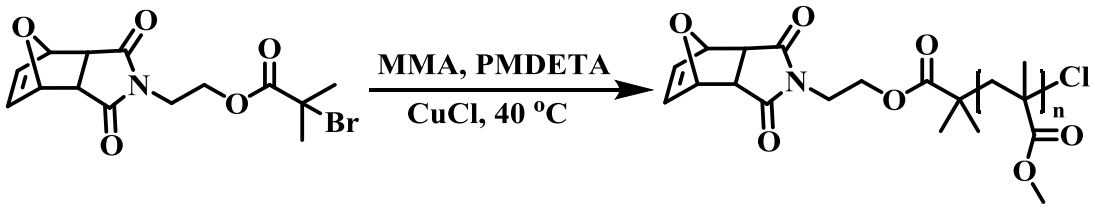


Figure 4.5 : Synthesis of MI-PMMA **(4).**

The NMR number-average molecular weight ($M_{n,\,NMR}$ = 2300 g/mol) was calculated from a ratio of the integrated values of OCH_3 of PMMA and N-CH_2 (δ 4 -3.2) to that of a signal at 6.5 ppm assignable to vinylic two protons, while being included the molecular weight of initiator (358.19 g/mol) (Figure 4.6). The number-average molecular weight obtained by GPC ($M_{n,\,GPC}$ = 2400 g/mol, relative to linear PMMA standards) is an excellent agreement with $M_{n,\,NMR}$, thus indicating that the quantitative maleimide end-group functionalization of the PMMA was successful. Moreover, M_w/M_n = 1.26 calculated from GPC displays narrow molecular weight distribution.

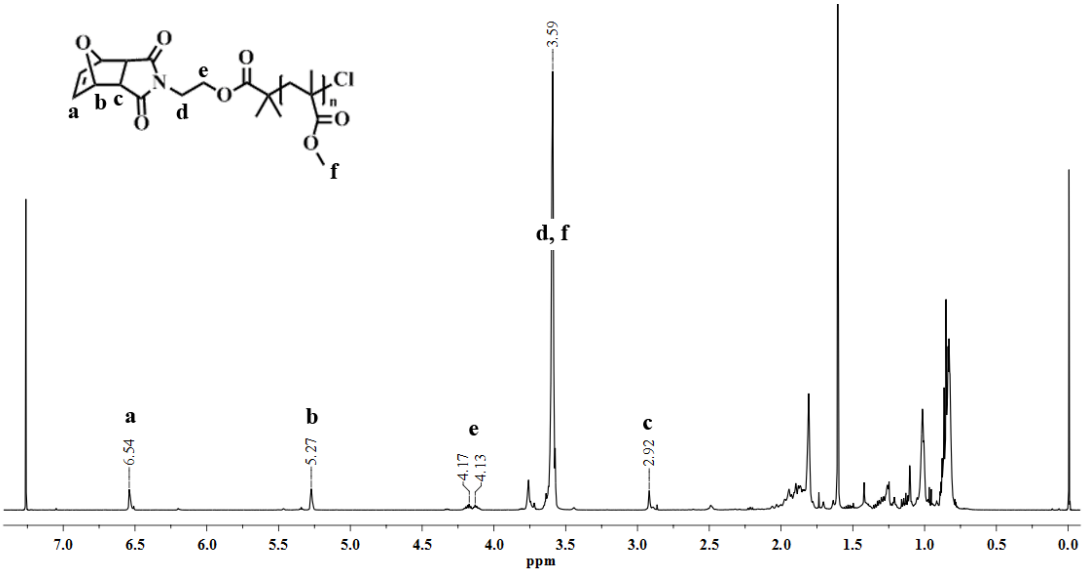


Figure 4.6 : ^{1}H NMR spectra of MI-PMMA in $CDCl_3$.

4.3 Preparation of Azide End Functional PEG and Benzyl Azide

Benzyl bromide converted to benzyl azide in water/acetone (1:4) mixture using NaN_3. Reaction mixture was stirred for 24 h at 60°C and compound **5** afforded as colorless oil (Figure 4.7).

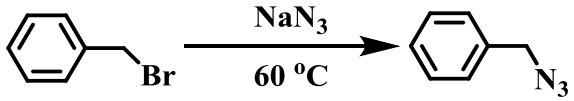


Figure 4.7 : Synthesis of benzyl azide **(5).**

From ^{1}H NMR spectra of 5 it was clearly seen that aromatic protons of benzyl detected between 7.42-7.31 ppm, methylene next to azide found at 4.35 ppm, and integrated values of this signals validated the number of protons on the molecule (Figure 4.8).

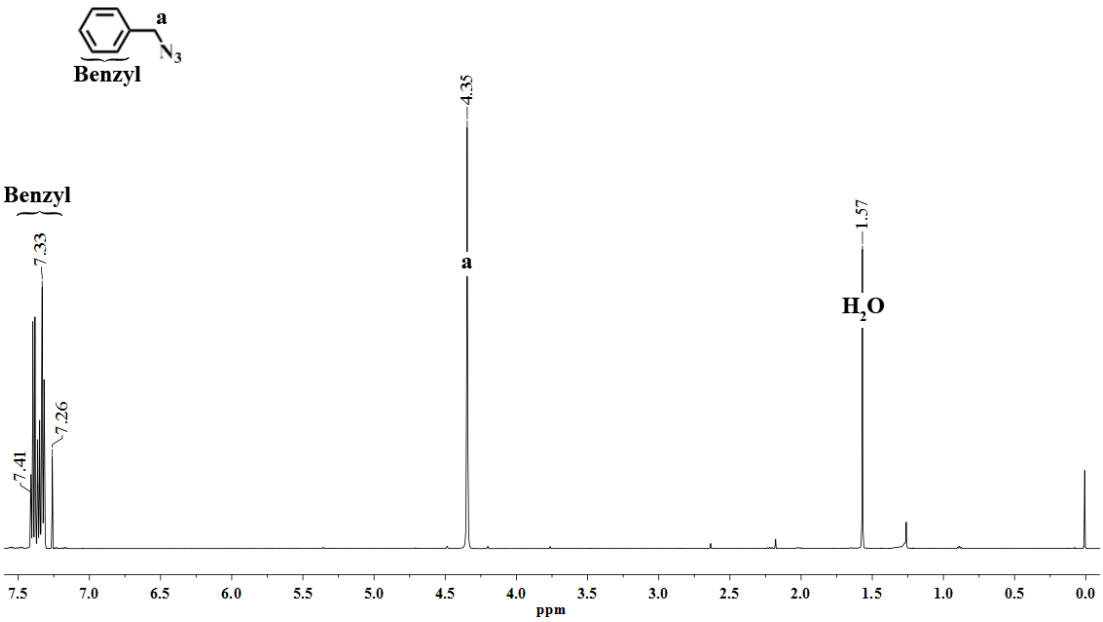


Figure 4.8 : ^{1}H NMR spectra of benzyl azide in $CDCl_3$.

Moreover poly(ethylene glycol) monomethyl ether was first tosylated using toluene-4-sulfonyl chloride and converted to azide by reacting NaN_3 in DMF at room temperature (Figure 4.9). After purification steps azide end functional PEG obtained as colorless viscous liquid.

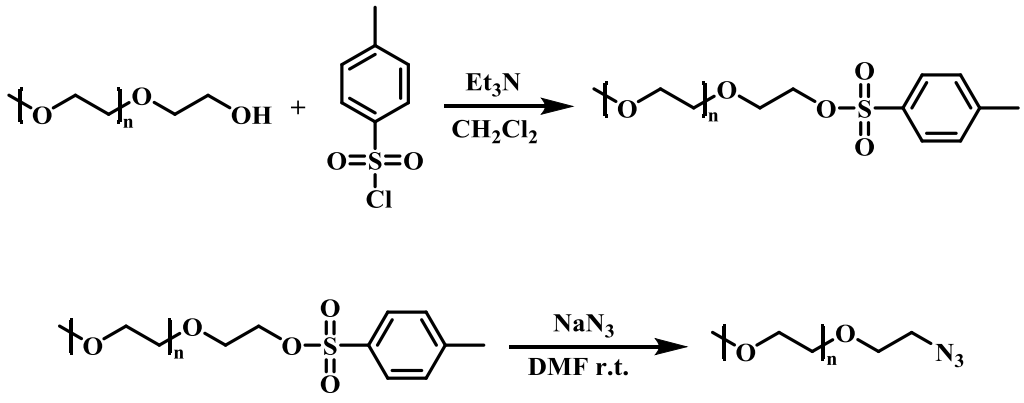


Figure 4.9 : Synthesis of azide end functional PEG (7).

The structure of azide end functional PEG (PEG-azide) confirmed via ^{1}H NMR spectroscopy (Figure 4.10). When PEG-OH was tosylated to obtain compound **6**, the signals originating from the C*H*$_2$O end group of the PEG-OH shifted from main peak of PEG-OH to 4.15 ppm after the conversion to PEG-azide this peak shifted back to main peak. Additionally Ar*H* (7.8-7.3 ppm) and methyl protons (2.44 ppm) of tosyl group disappeared from the spectrum. The $M_{n,NMR}$ was determined by comparing the integral of methyl end group of PEG-azide signal (δ 3.36) to those of repeating unit of PEG-azide (δ 3.68-3.51), while including the MW of azide functionality. $M_{n,NMR}$ fit well with the $M_{n,theo}$ indicating a quantitative azide end-group functionalization.

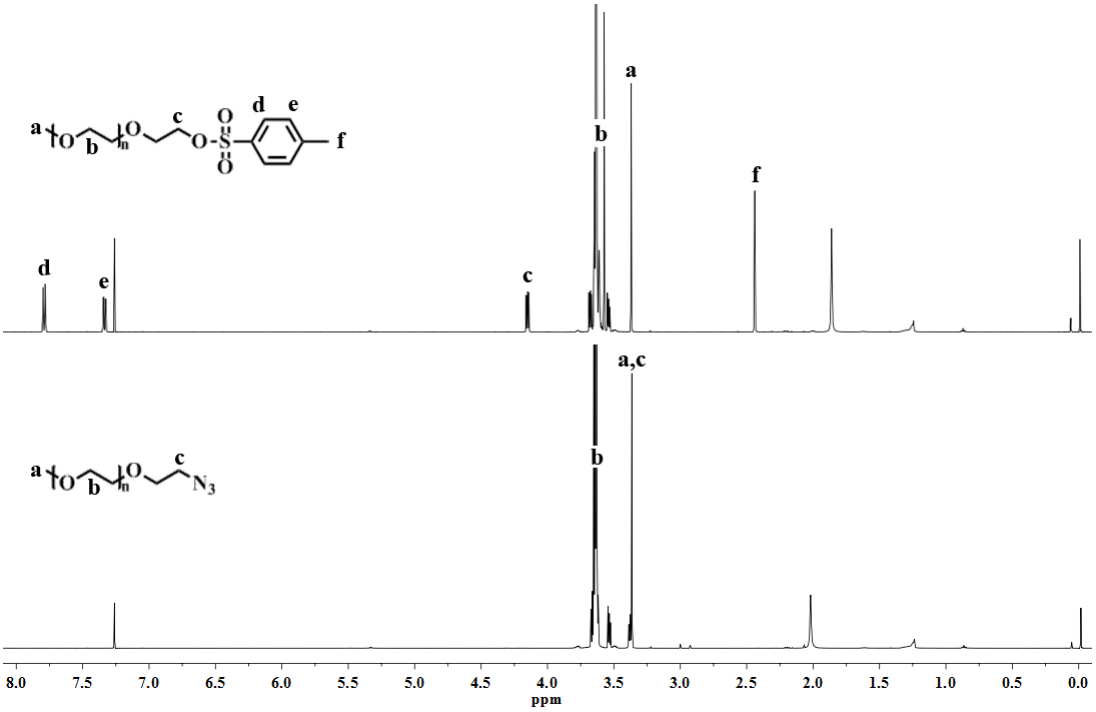


Figure 4.10 : ^{1}H NMR spectra of tosylated PEG **(6)** and PEG-azide **(7)** in $CDCl_3$.

4.4 Preparation of Functional Diol Monomers

2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(8)** was synthesized by the reaction of 2,2-bis(hydroxymethyl)propionic acid with 2,2-dimethoxypropane in dry acetone in the presence of *p*-toluene sulfonic acid as catalyst. Reaction is is given below schematically (Figure 4.11).

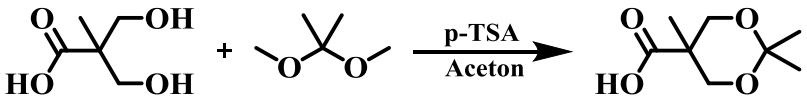


Figure 4.11 : Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(8)**.

Subsequent esterification reaction between 9-anthracene methanol and **8** was carried out using DCC as a coupling agent and catalytic amount of DMAP as catalyst to give anthracen-9ylmethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(9)**. Process is given below schematically (Figure 4.12).

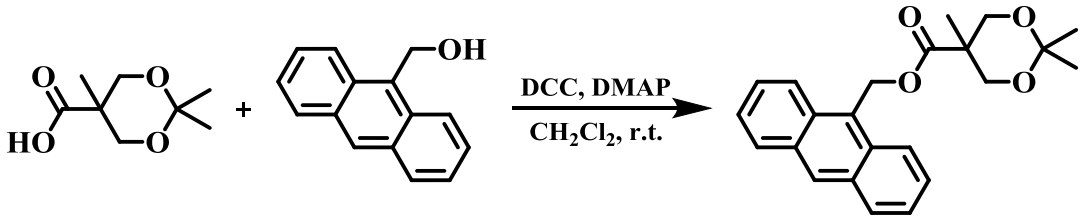


Figure 4.12 : Synthesis of anthracen-9ylmethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(9)**.

Then, hydrolysis of compound **9** was taken placed in THF using 1 M HCl to produce anthracen-9-yl methyl 3-hydroxy-2-(hydroxymethyl)-2-methyl propanoate (anthracene diol) **(10)**, the reaction was conducted in room temperature for 2 h. Procedure of the reaction is given below schematically (Figure 4.13).

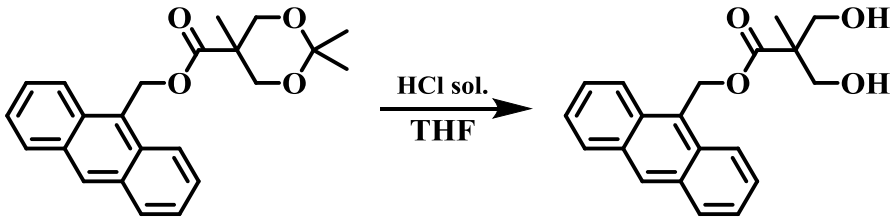


Figure 4.13 : Synthesis of anthracene diol **(10)**.

The ^{1}H NMR spectrums of the **8**, **9** and **10** are shown in Figure 4.14. From the NMR spectrum, the peaks in the range between 4.17 and 3.67 ppm are assigned to methylene protons. The peaks in the range between 1.42 and 1.10 ppm are identified to methyl protons, when hydrolysis of **9** have conducted the peaks at 1.39 and 1.37 ppm disappeared. From the NMR spectrum, the new signals which Ar*H* of anthracene of **5** and **6** appeared between 8.51 and 7.47 ppm. Another new peak of methylene protons next to anthracene functionality formed after the synthesis of **5** at 6.2 ppm. The data derived from the NMR spectrums confirmed that preparation of anthracene diol carried out successfully.

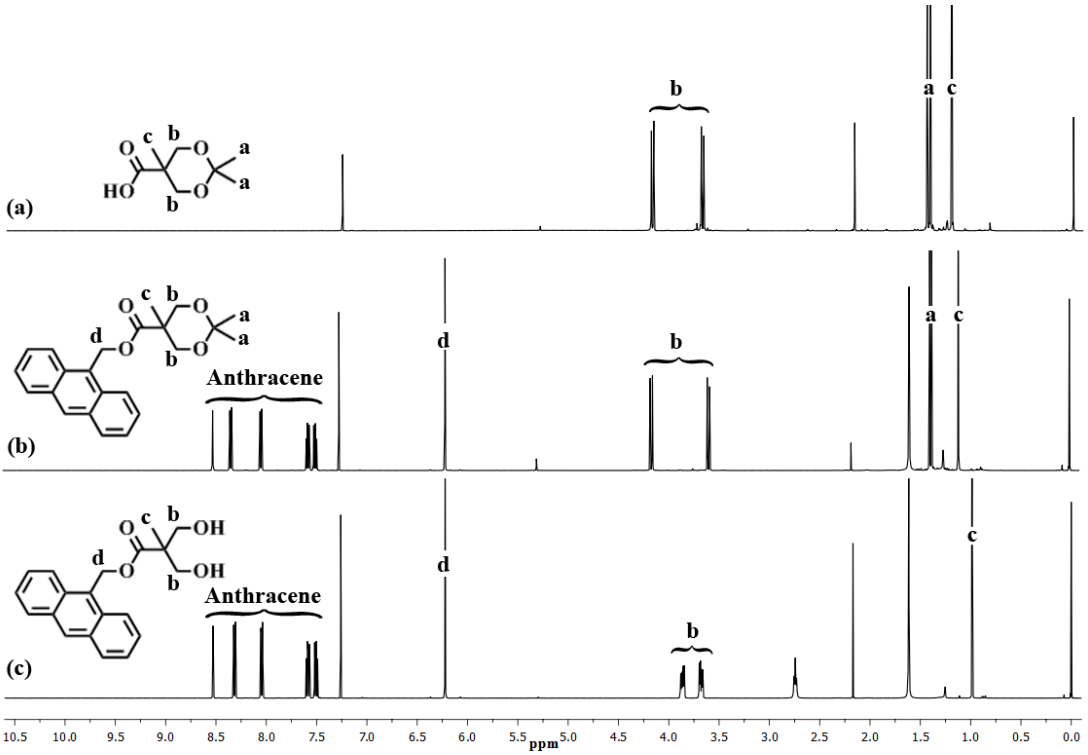


Figure 4.14 : ^{1}H NMR spectra of: **a)** 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(8)**, **b)** anthracen-9-ylmethyl 2,2,5-trimethyl-1,3-dioxane-5 carboxylate **(9)**, **c)** anthracen-9-yl methyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (anthracene diol) **(10)**, in $CDCl_3$.

Synthesis of alkyne diol consist two additional reaction. First reaction was started with esterification reaction between propargyl alcohol and **8** which was carried out using DCC as a coupling agent and catalytic amount of DMAP as catalyst to give prop-2-yn-1-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(11)**. Process is given below schematically (Figure 4.15).

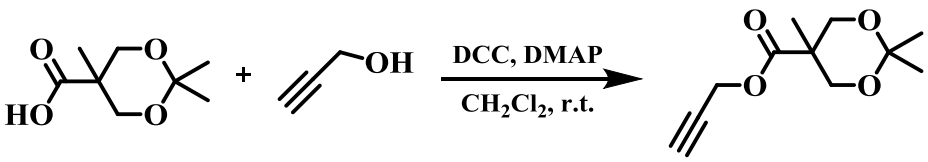


Figure 4.15 : Synthesis of prop-2-yn-1-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(11)**.

Then, hydrolysis of compound **11** was taken placed in THF using 1 M HCl to produce prop-2-yn-1-yl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (alkyne diol) **(12)**, the reaction was conducted in room temperature for 2 h. Procedure of the reaction is given below schematically (Figure 4.16).

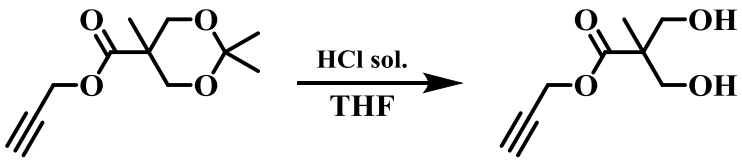


Figure 4.16 : Synthesis of alkyne diol **(12)**.

The ^{1}H NMR spectrums of the **8**, **11** and **12** are shown in Figure 4.17. From the NMR spectrum, the peaks in the range between 4.18 and 3.64 ppm are assigned to methylene protons. The peaks in the range between 1.42 and 1.10 ppm are identified to methyl protons, when hydrolysis of **11** have conducted the peaks at 1.41 and 1.37 ppm disappeared. From the NMR spectrum, the new signals of **11** and **12** appeared which methine proton of alkyne 2.46 and 2.49 ppm and methylene protons next to alkyne group at 4.73 and 4.72 ppm. The data derived from the NMR spectrums confirmed that preparation of alkyne diol carried out successfully.

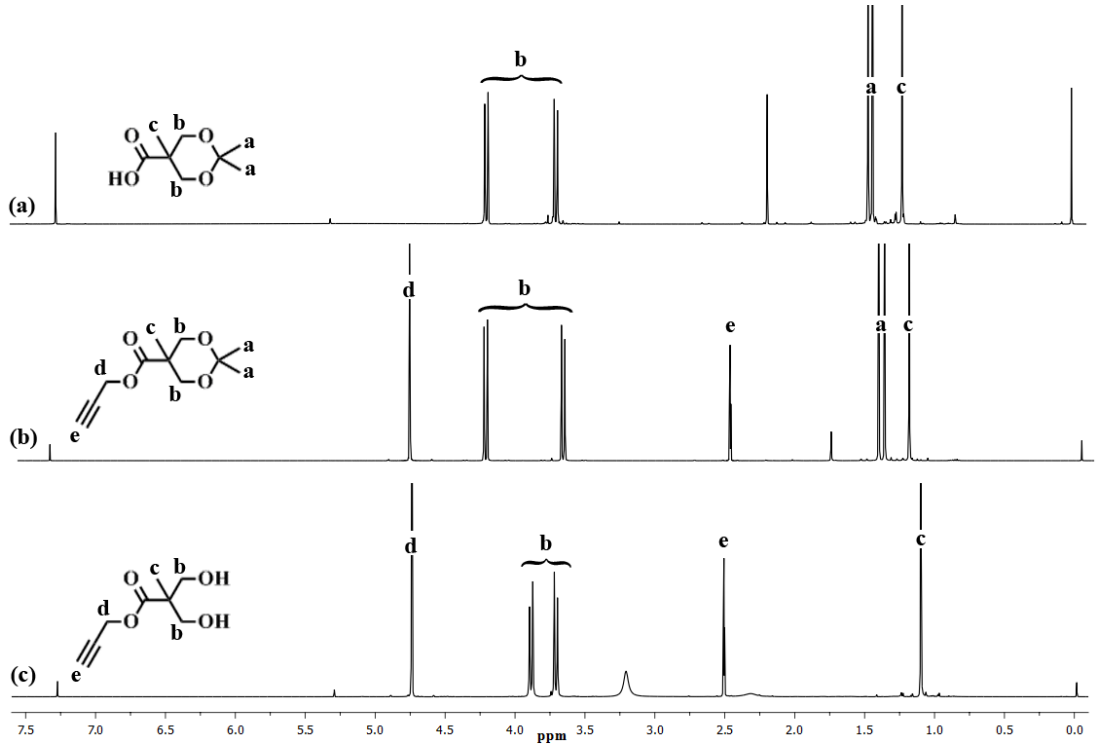


Figure 4.17 : ^{1}H NMR spectra of: **a)** 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(8)**, **b)** prop-2-yn-1-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(11)**, **c)** prop-2-yn-1-yl 3-hydroxy-2-(hydroxymethyl)-2-methyl propanoate (alkyne diol) **(12)**, in $CDCl_3$.

Further, synthesis of perfluorophenyl diol consist two additional reaction. First reaction was started with esterification reaction between 2,3,4,5,6-pentafluorophenol and **8** which was carried out using DCC as a coupling agent and catalytic amount of

DMAP as catalyst to give perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(13)**. Process is given below schematically (Figure 4.18).

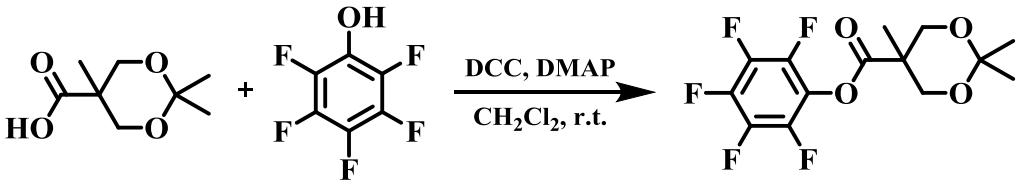


Figure 4.18 : Synthesis of perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(13)**.

The second reaction for synthesis of perfluorophenyl diol is hydrolysis of compound **11**, which was taken placed in THF using 1 M HCl to produce perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (perfluorophenyl diol) **(14)**, the reaction was conducted in room temperature for 2 h. Procedure of the reaction is given below schematically (Figure 4.19).

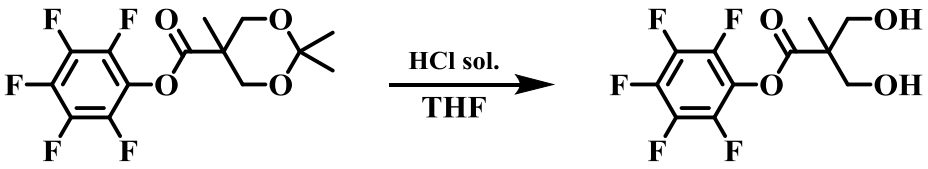


Figure 4.19 : Synthesis of perfluorophenyl diol **(14)**.

The ^{1}H NMR and ^{19}F NMR spectrums of the **8**, **13** and **14** are shown in Figure 4.20 and Figure 4.21. From the ^{1}H NMR spectrum, the peaks in the range between 4.33 and 3.67 ppm are assigned to methylene protons. The peaks in the range between 1.48 and 1.31 ppm are identified to methyl protons, when hydrolysis of **13** have conducted the peaks at 1.48 and 1.43 ppm disappeared. From the ^{19}F NMR spectrum, the new signals of **11** and **12** appeared which F signals of F substituted phenyl group were found at -152 (o-*F*), -157 (p-*F*) and -162 (m-*F*) ppm. The data derived from the ^{1}H NMR and ^{19}F NMR spectrums confirmed that preparation of perfluorophenyl diol carried out successfully.

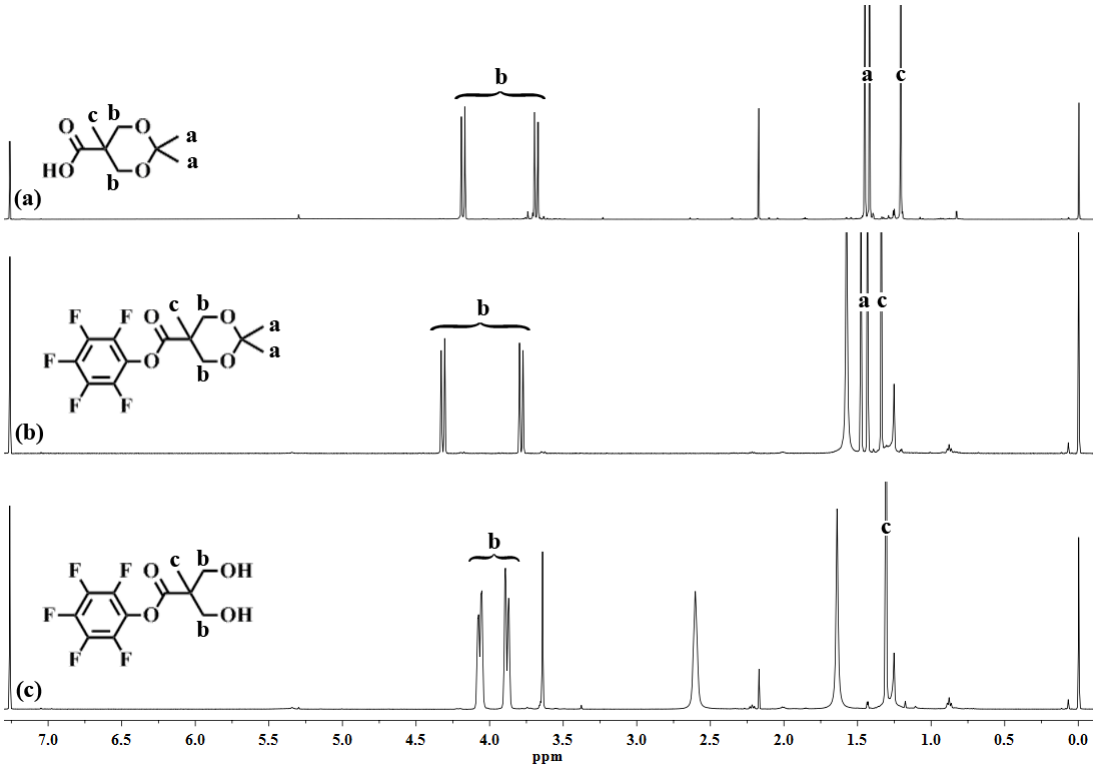


Figure 4.20 : ^{1}H NMR spectra of: **a)** 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(8)**, **b)** perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(13)**, **c)** perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (perfluorophenyl diol) **(14)**, in $CDCl_3$.

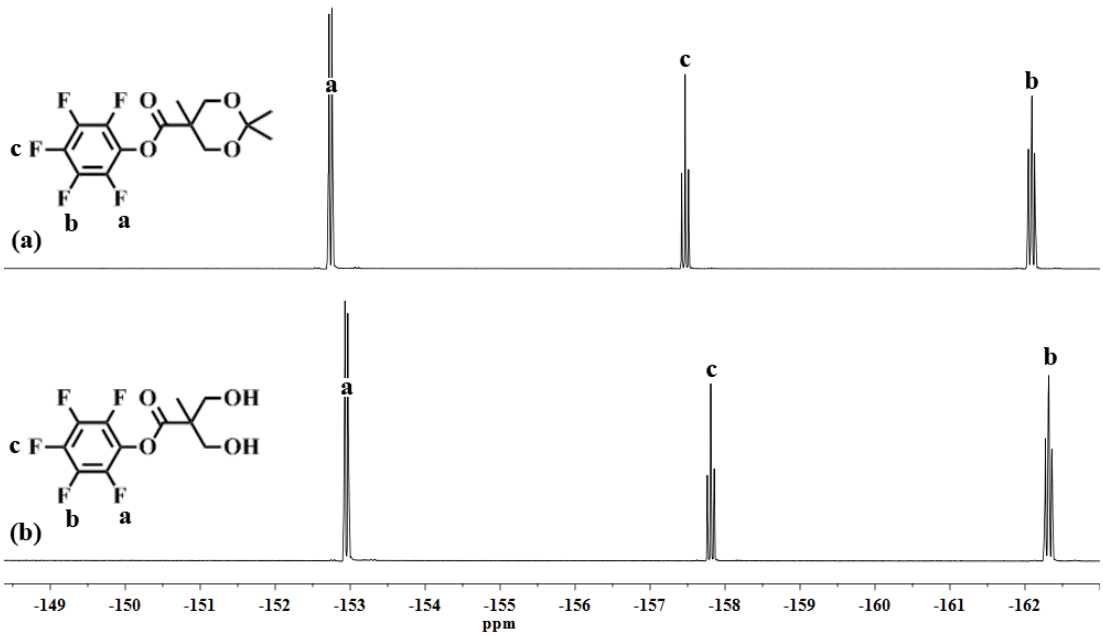


Figure 4.21 : ^{19}F NMR spectra of: **a)** perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(13)**, **b)** perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (perfluorophenyl diol) **(14)**, in $CDCl_3$.

4.5 Preparation of PU-(anthracene-*co*-alkyne) (15) and PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) (16)

The linear PU with regular pendant anthracene and alkyne functional groups PU-(anthracene-*co*-alkyne) **(15)** was synthesized by step-growth polymerization of anthracene diol, **10**, alkyne diol, **12** and HMDI using DBTDL as the catalyst in CH_2Cl_2 at room temperature for 10 days. Procedure of the reaction is given below schematically (Figure 4.22).

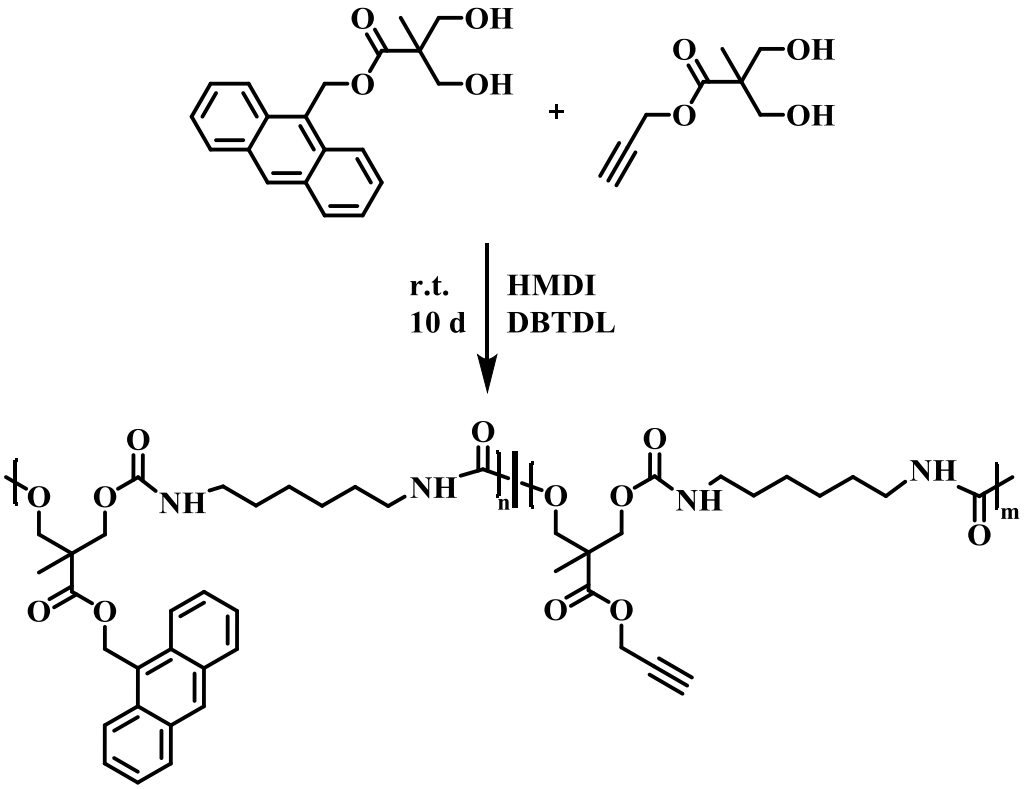


Figure 4.22 : Synthesis of PU-(anthracene-*co*-alkyne), **(15)**.

^{1}H NMR spectroscopy confirmed the expected structure of the PU-(anthracene-*co*-alkyne) primarily displaying the characteristic signals of the Ar*H*s of anthracene between 8.48-7.43 ppm, methine protons of alkyne at 2.47 ppm and the C*H*$_2$NHC=O of PU backbone at 3.20–2.90 ppm (Figure 4.23). The ratio of alkyne and anthracene functionalities was found by the integrated ratio of the Ar*H*s of anthracene unit at 8.48 ppm and the methine protons of alkyne at 2.47 ppm which anthracene and alkyne ratio was found to be 0.58:0.42 respectively, indicating the successful formation of the PU-(anthracene-*co*-alkyne). GPC analysis exhibited: $M_{n,GPC}$=11088 g/mol, M_w/M_n=1.28 relative to PS standards in THF at 30°C.

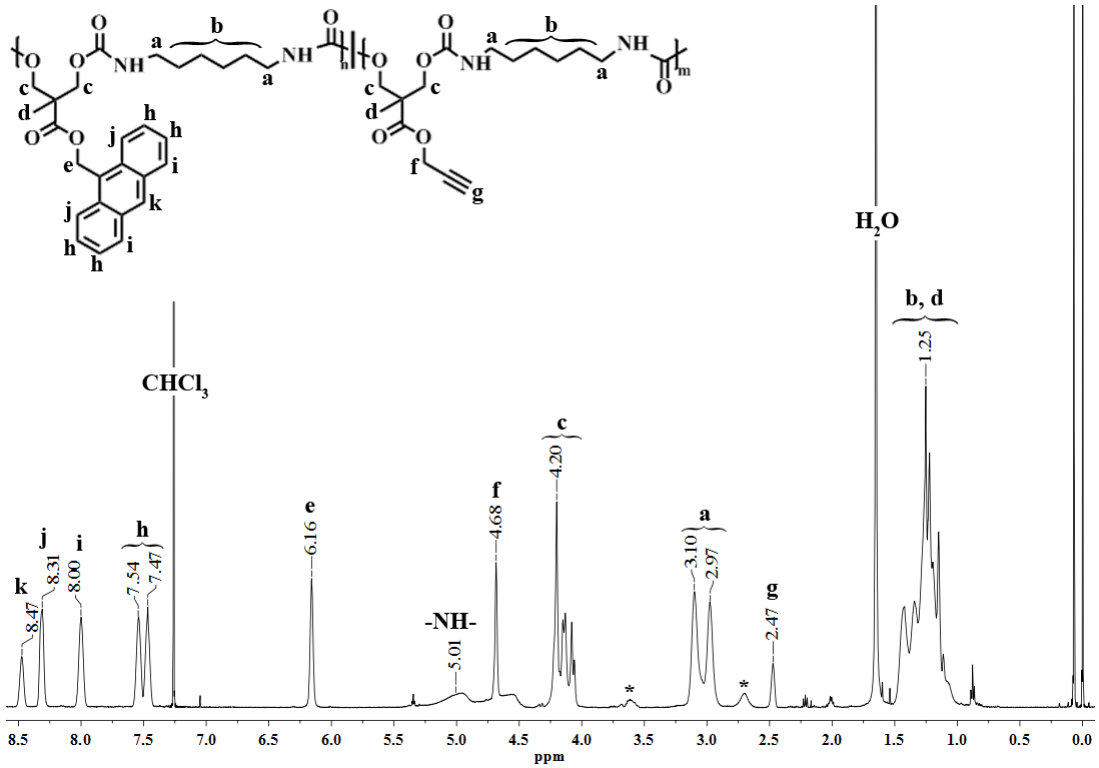


Figure 4.23 : ^{1}H NMR spectra of PU-(anthracene-*co*-alkyne), **(16),** in $CDCl_3$.

The linear PU with regular pendant anthracene, alkyne and perfluorophenyl functional groups PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) **(16)** was synthesized by step-growth polymerization of anthracene diol, **10**, alkyne diol, **12**, perfluorophenyl diol, **14** and HMDI using DBTDL as the catalyst in CH_2Cl_2 at room temperature for 10 days. Procedure of the reaction is given below schematically (Figure 4.24).

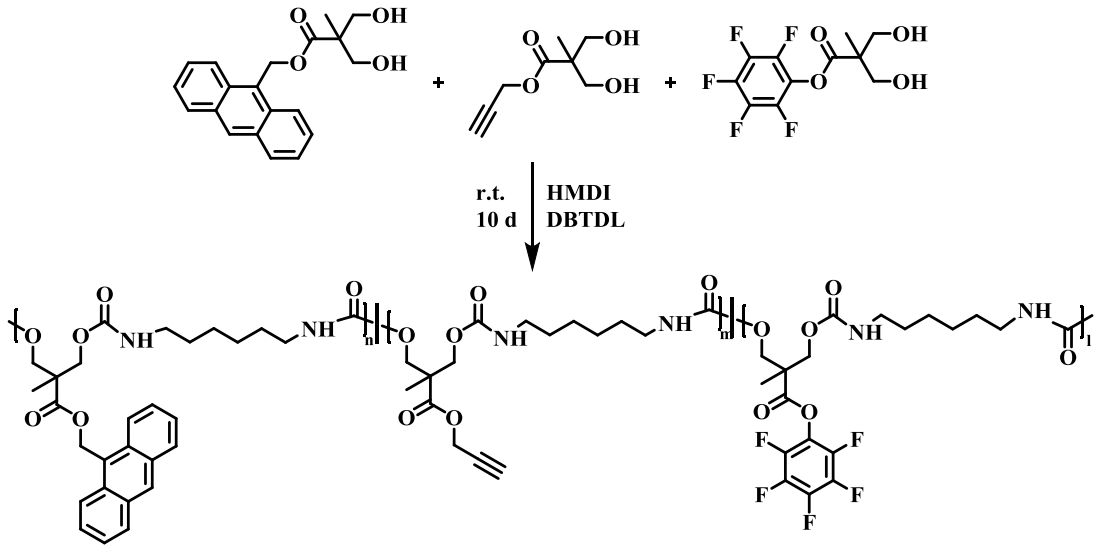


Figure 4.24 : Synthesis of PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl), **(16)**.

^{1}H NMR spectroscopy confirmed the expected structure of the PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) primarily displaying the characteristic signals of the Ar*H*s of anthracene between 8.48-7.43 ppm, methine protons of alkyne at 2.47 ppm and the C*H*$_2$NHC=O of PU backbone at 3.20–2.90 ppm (Figure 4.25). On the other hand, perfluorophenyl group has no specific protons separated from other signals, despite F signals. ^{19}F NMR spectroscopy (Figure 4.26) confirmed the expected o-, m- and p- substituted fluorine signals, the integrated ratio of signals was found to be 2:2:1 respectively. The ratio of functionalities was found by the integrated ratio of the Ar*H*s of anthracene unit at 8.48 ppm, the methine protons of alkyne at 2.47 ppm and diols C*H*$_2$OC=O protons between 4.43-4.03 ppm, which anthracene, alkyne and perfluorophenyl ratio was found to be 0.44:0.28:0.28 respectively, indicating the successful formation of the PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl). GPC analysis exhibited: $M_{n,\,GPC}$=15600 g/mol, M_w/M_n=1.37 relative to PS standards in THF at 30°C.

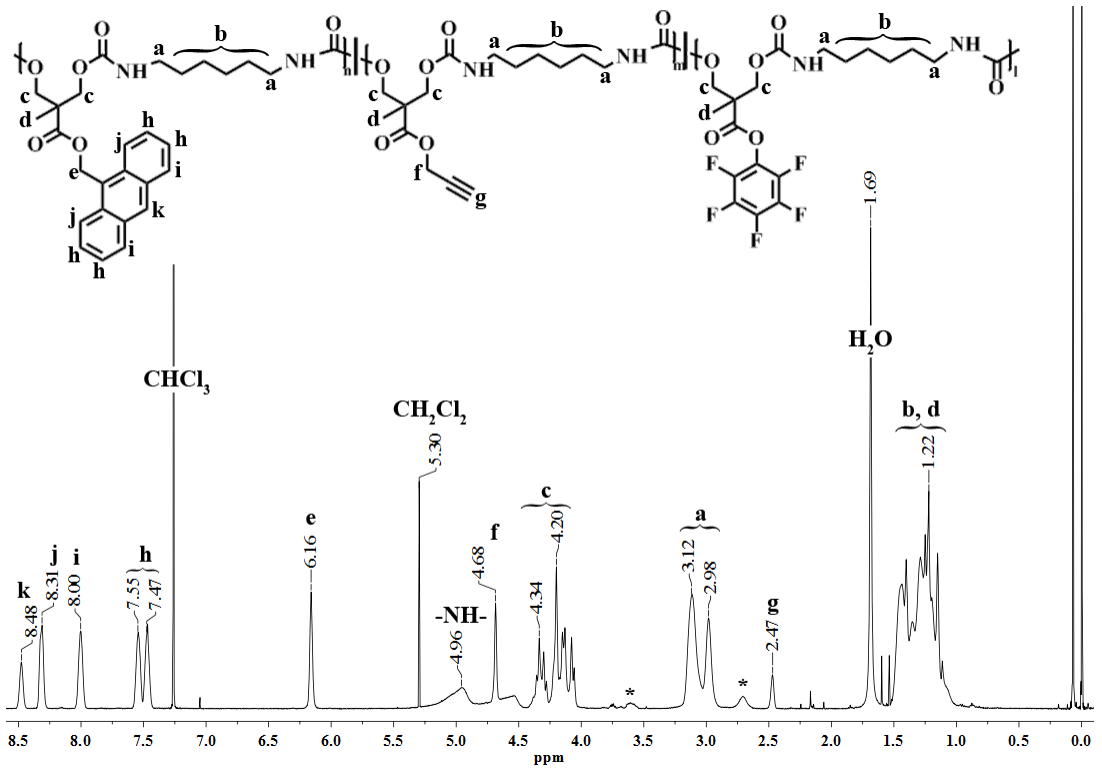


Figure 4.25 : ^{1}H NMR spectra of PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl), **(16),** in $CDCl_3$.

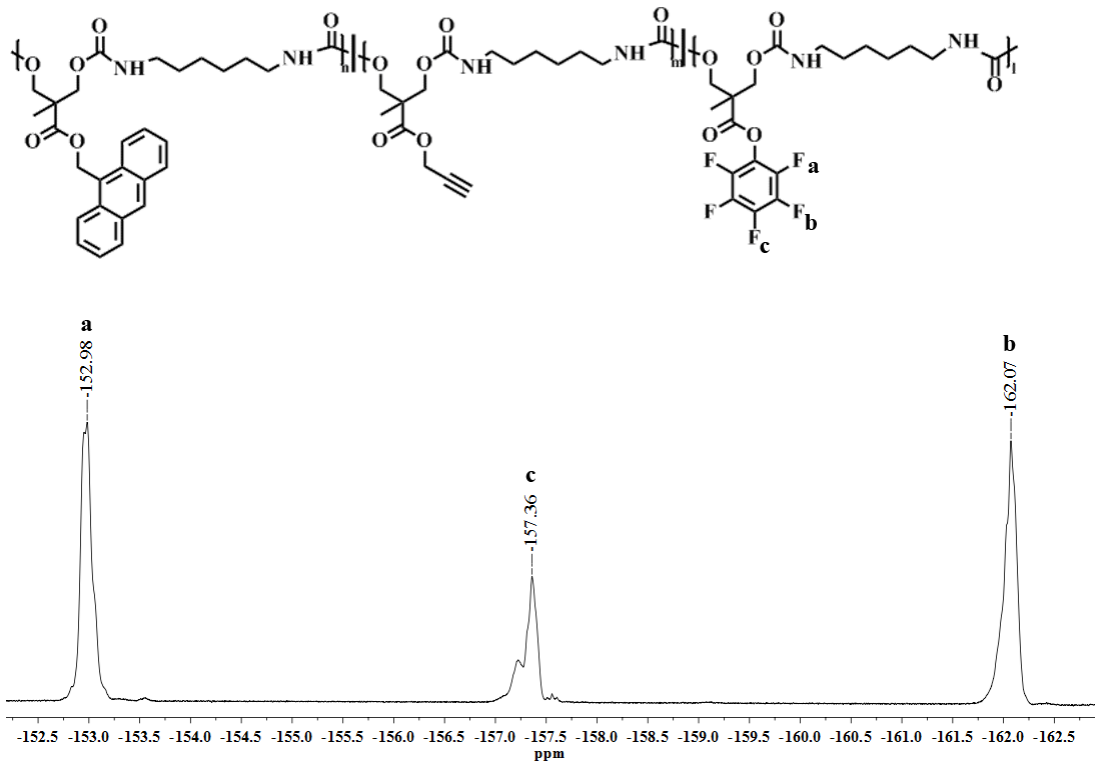


Figure 4.26 : ^{19}F NMR spectra of PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl), **(16)** in $CDCl_3$.

4.6 Modification of PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl), (16) via Click Reactions

The CuAAC click reaction between **16** and benzyl azide, **5** was conducted in DMF in the presence of CuBr/PMDETA at room temperature for 24 h (Figure 4.27). After the specified time, reaction mixture was diluted with THF, filtered through neutral alumina to remove copper complex, and precipitated in methanol. After these treatments, resulting polymer, **(17)** characterized by ^{1}H, ^{19}F NMR and GPC measurements.

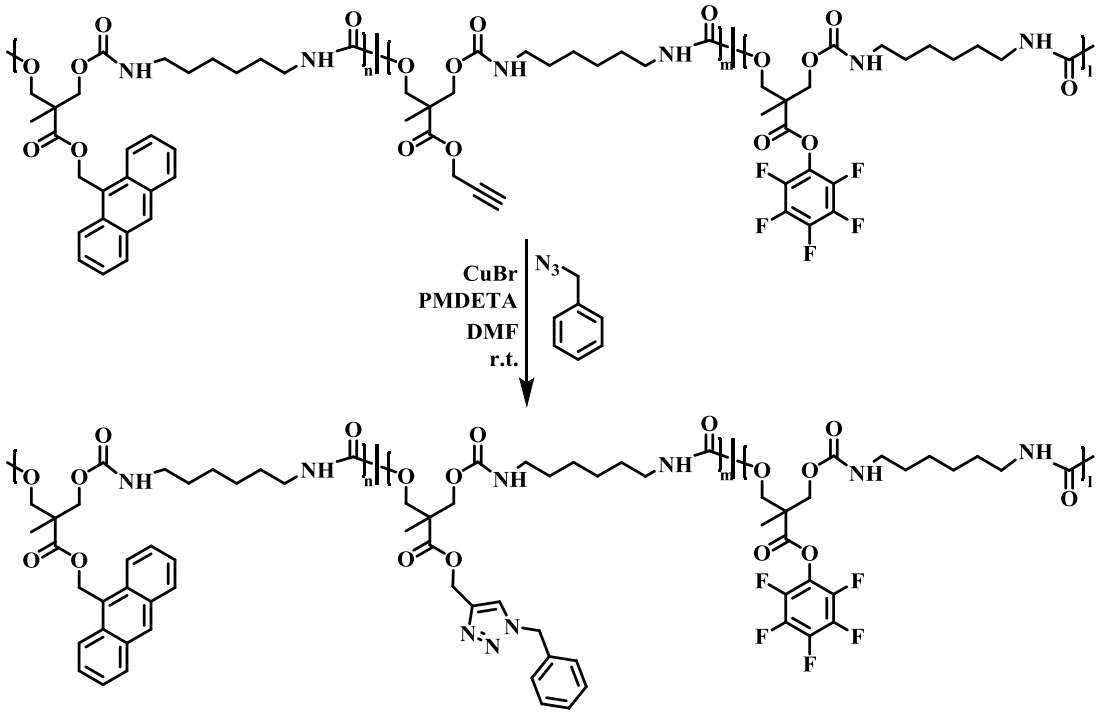


Figure 4.27 : CuAAC click reaction between **16** and benzyl azide.

^{1}H NMR spectroscopy confirmed the expected structure of the compound **17** primarily displaying the characteristic signals of the Ar*H*s of anthracene and methine protons of triazole between 8.48-7.43 ppm, Ar*H*s of benzyl group between 7.37-7.19 ppm, methylene protons adjacent to benzyl group at 5.19 ppm (Figure 4.28). In addition, complete disappearance of methine protons of alkyne at 2.47 ppm and the shift of methylene protons from 4.68 ppm to 5.49 ppm indicates successful preparation of compound **17**. As seen from Figure 4.29 ^{19}F NMR spectroscopy was not changed after the reaction. GPC analysis exhibited: $M_{n,\,GPC}$=15360 g/mol, M_w/M_n=1.15 relative to PS standards in THF at 30°C.

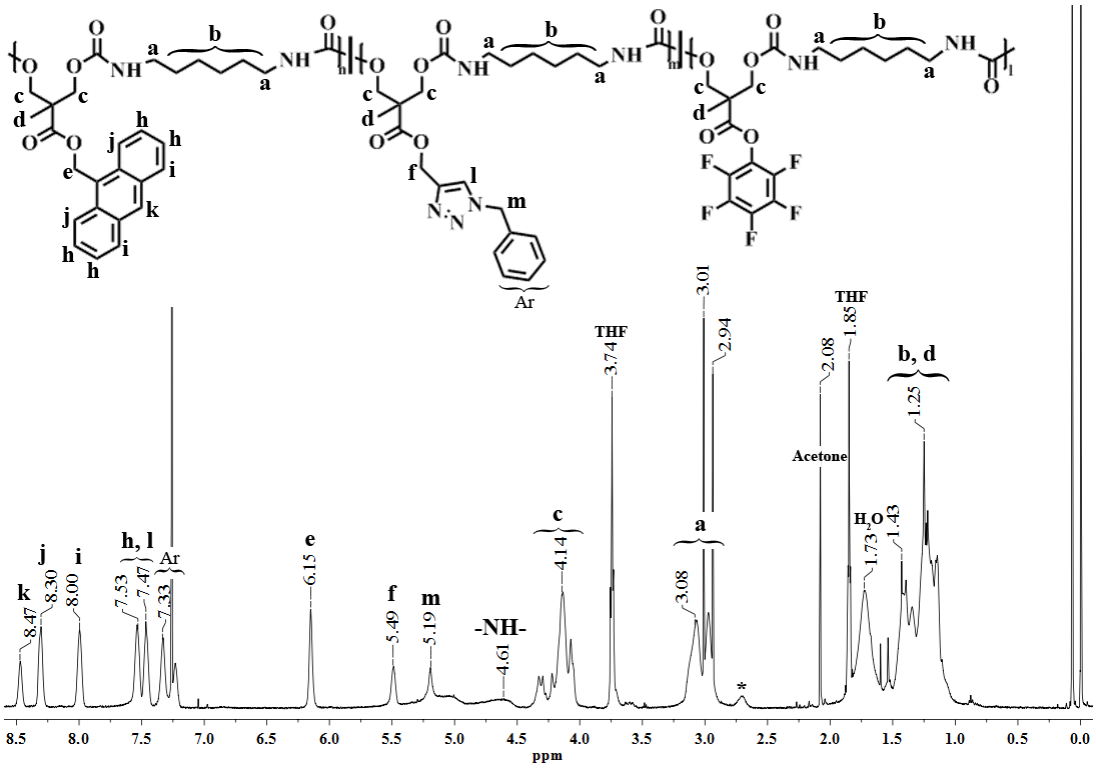


Figure 4.28 : ^{1}H NMR spectra of **17**, in $CDCl_3$.

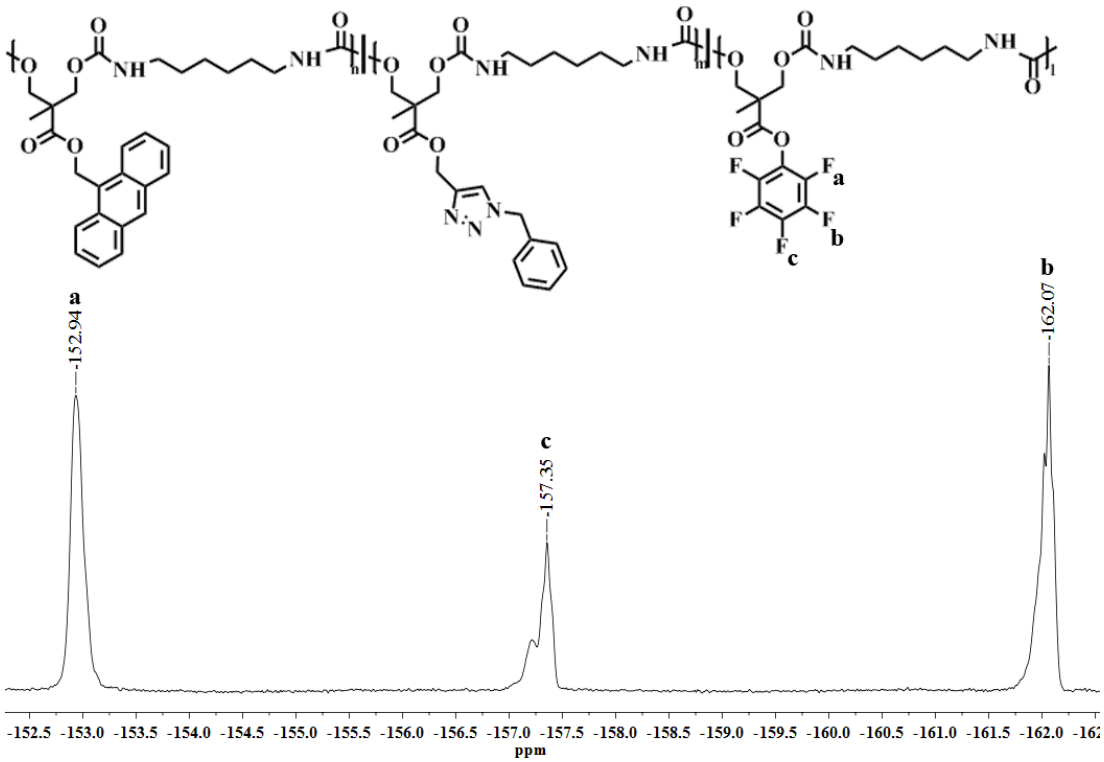


Figure 4.29 : ^{19}F NMR spectra of **17**, in $CDCl_3$.

Secondly, pendant perfluorophenyl ester functionality of **17** was reacted with octylamine to give **18** in the presence of TEA in THF (Figure 4.30). The substitution

reaction was conducted at room temperate for 24 h. After the specific time reaction mixture precipitated in methanol.

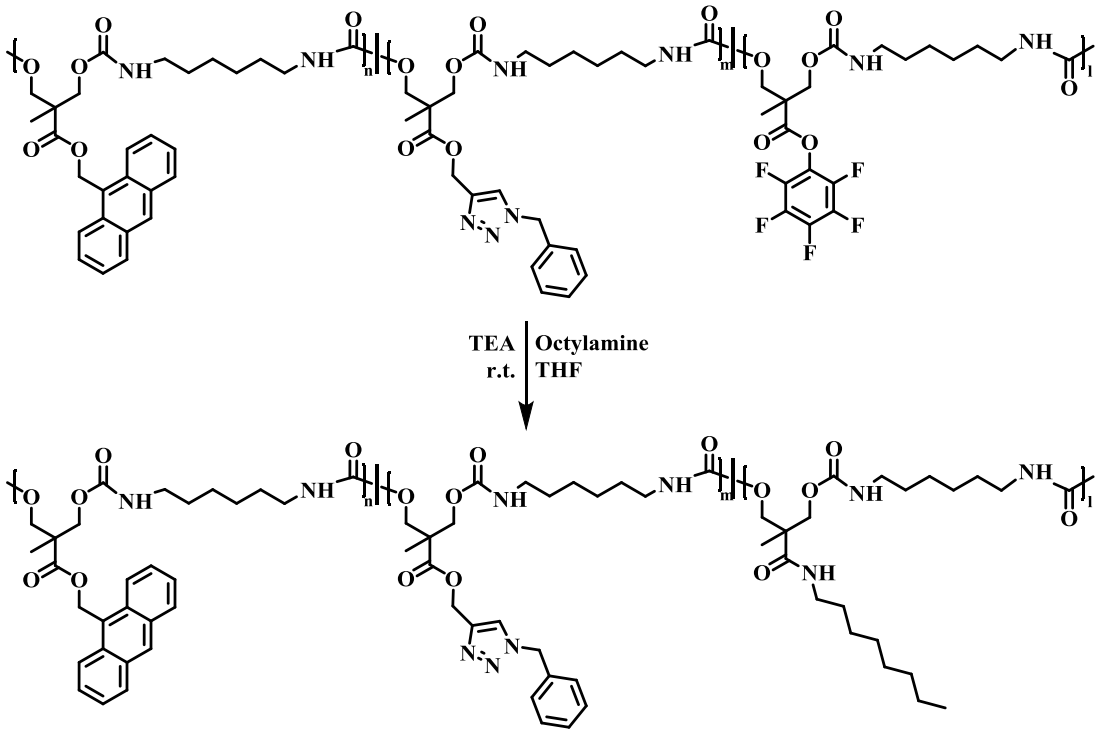


Figure 4.30 : Synthesis of **18** via active ester reaction.

^{1}H NMR spectroscopy confirmed the expected structure of the compound **18** primarily displaying the characteristic signals of the Ar*H*s of anthracene and methine protons of triazole between 8.48-7.43 ppm, Ar*H*s of benzyl group between 7.37-7.20 ppm, methylene protons adjacent to benzyl group at 5.19 ppm (Figure 4.31). ^{1}H NMR revealed the appearance of new signal regarding methyl protons of octylamine between 0.9 and 0.8 ppm. In addition, ^{19}F NMR spectroscopy of compound **18** confirmed the complete disappearance of fluorine signal of perfluorophenyl group, which indicates successful preparation of compound **18** (Figure 4.32). GPC analysis exhibited: $M_{n,\,GPC}$=16320 g/mol, M_w/M_n=1.17 relative to PS standards in THF at 30°C.

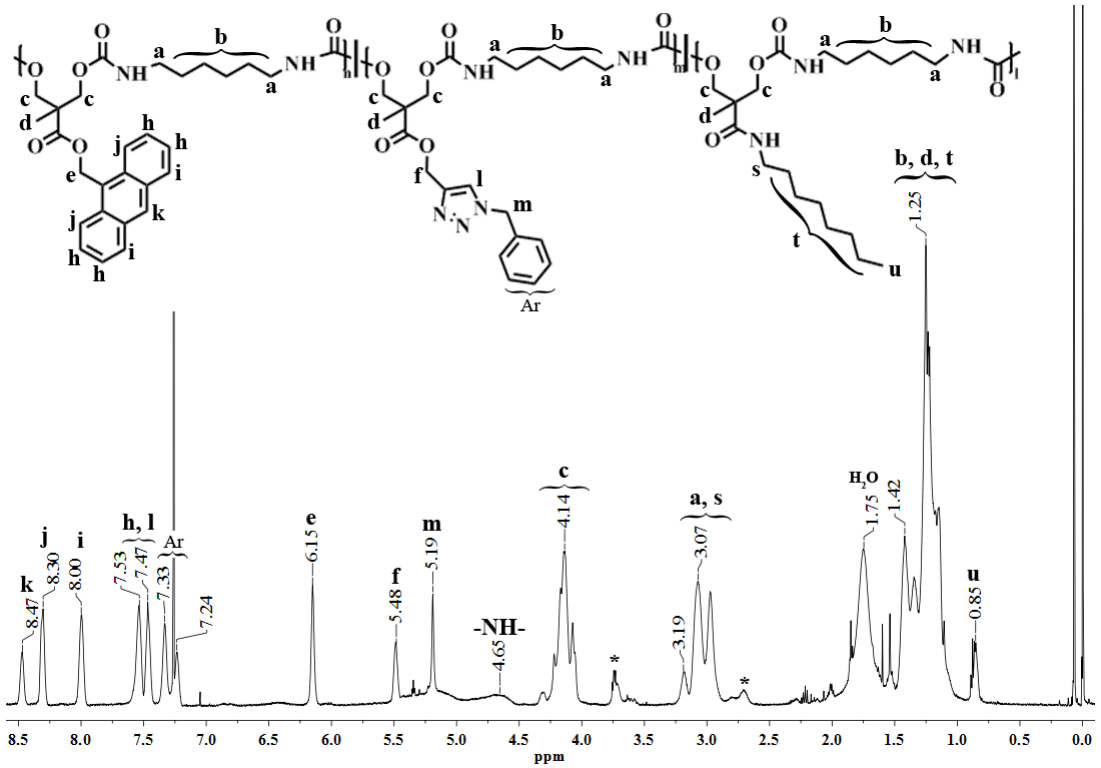


Figure 4.31 : ^{1}H NMR spectra of **18**, in $CDCl_3$.

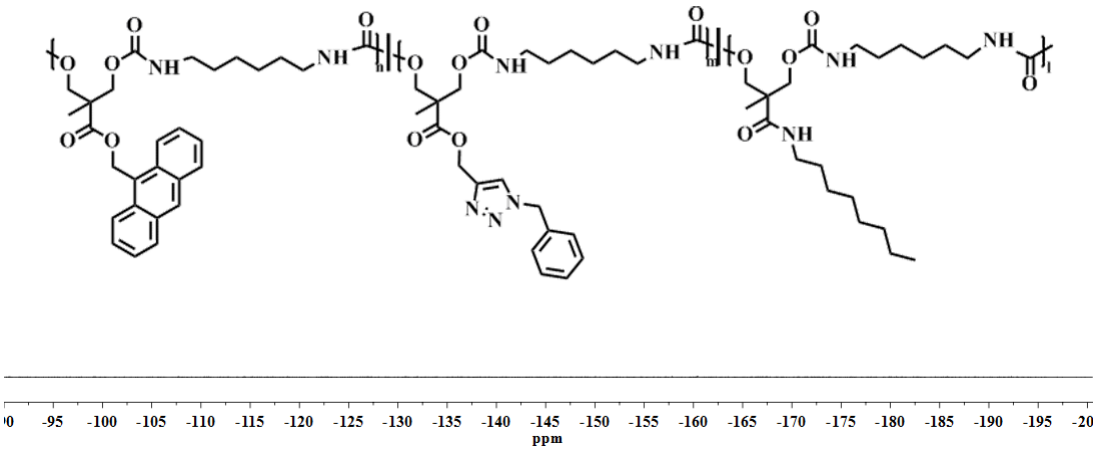


Figure 4.32 : ^{19}F NMR spectra of **18**, in $CDCl_3$.

Lastly, Diels-Alder reaction was performed with pendant anthracene functional PU, **18** and 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.02,6]dec-8-ene-3,5-dione, **2** to obtain compound **19** in dioxane/toluene mixture (2:1, vol/vol) at 105°C for 48 h (Figure 4.33). After the specific time reaction mixture precipitated in methanol. The DA reaction monitored by UV-Vis spectroscopy following the disappearance of the characteristic five-finger absorbance of the anthracene at 300–400 nm. The efficiency of DA reaction calculated by the following equation **(4.1)** and absorption values, which

were used for efficiency calculations, depends on the maximum absorption of anthracene at 367 nm.

$$DA_{eff}\% = \left[1 - {}^{A_{48}}/_{A_0}\right] \times 100 \qquad \textbf{4.1}$$

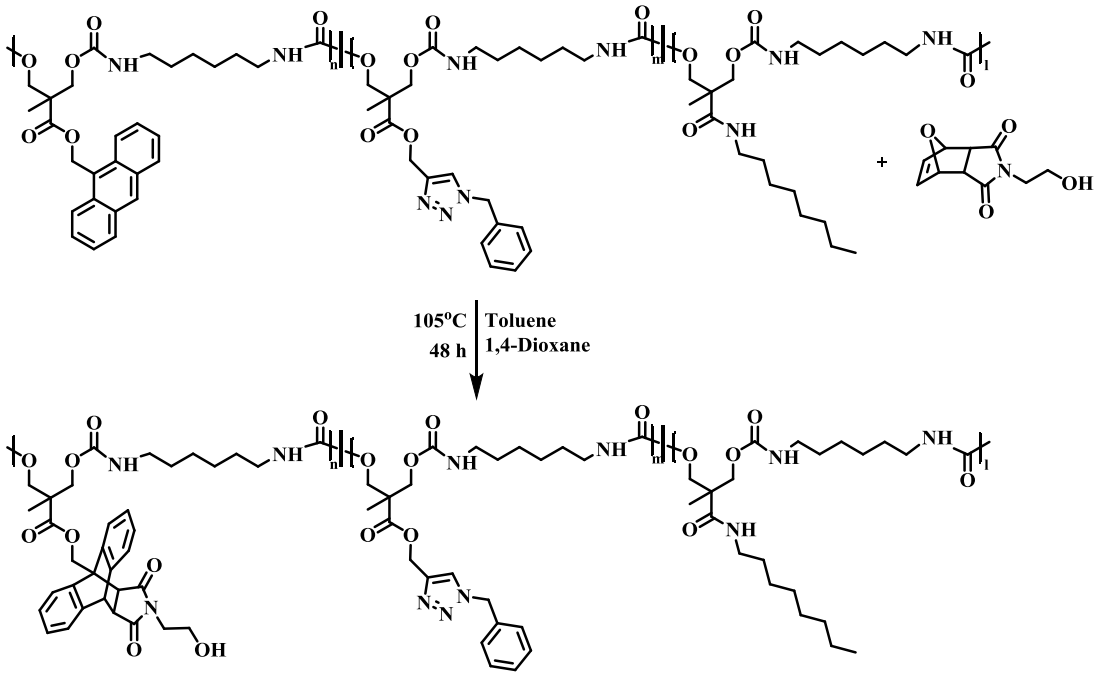


Figure 4.33 : Synthesis of **19** via Diels-Alder reaction.

From the UV-Vis spectroscopy, DA reaction efficiency was found to be 92%, according to maximum absorption values of anthracene at 367 nm (Figure 4.34).

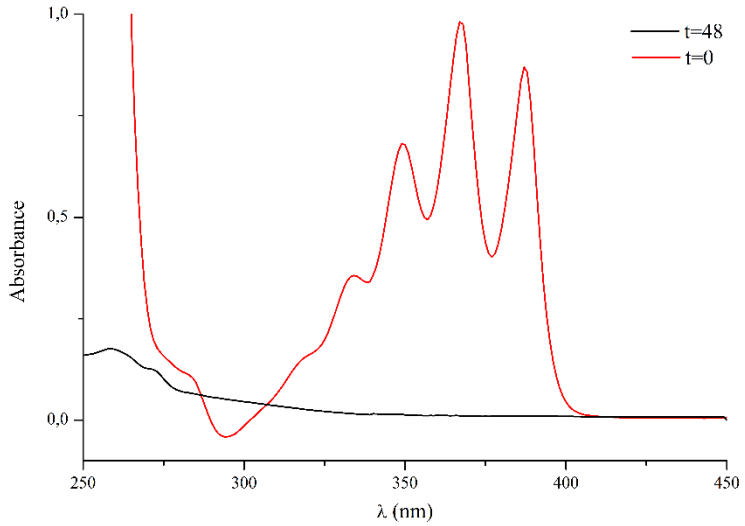


Figure 4.34 : UV-Vis spectra of DA reaction of **18** and **2**.

^{1}H NMR spectroscopy confirmed the expected structure of the compound **19** primarily displaying the characteristic signals of the Ar*H*s of aromatic groups between 7.44-7.08 ppm, methine protons of triazole 7.58 ppm and methyl protons of octylamine between 0.92-0.8 ppm (Figure 4.35). ^{1}H NMR revealed the appearance of new signal regarding methine bridge head protons at 4.77 ppm, the characteristic signals of **2** and Diels-Alder adduct. In addition, ^{1}H NMR spectroscopy of compound **19** confirmed the complete disappearance of Ar*H*s of anthracene between 8.5-7.5 ppm, which indicates successful preparation of compound **19**.

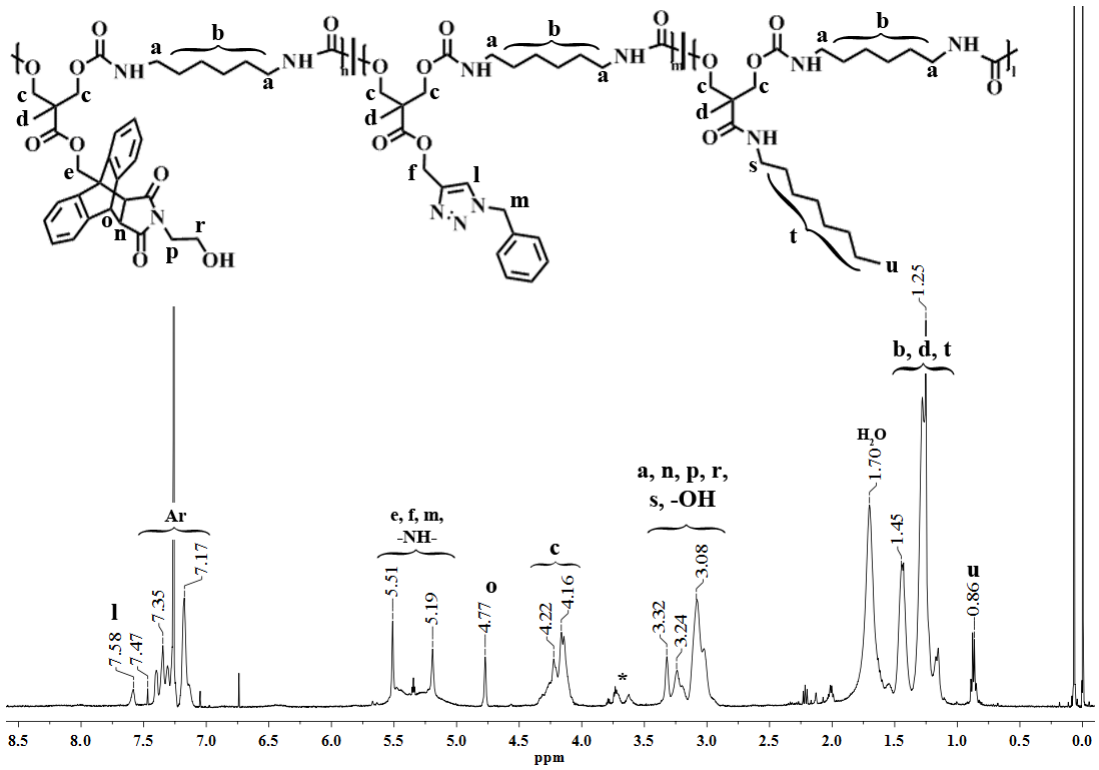


Figure 4.35 : ^{1}H NMR spectra of **19**, in $CDCl_3$.

After CuAAC, DA and active ester substitution reaction a clear shift to the higher molecular weight region was detected from GPC measurements while maintaining narrow polydispersity index (M_w/M_n), except for the CuAAC product **17**, in which a negligible change to the lower molecular weight occurred (Figure 4.36, Table 4.1).

Table 4.1 : The results of PU-(Anthracene-*co*-Alkyne-*co*-Perfluorophenyl) modifications.

Polymer	$M_{n,GPC}$[a] (g/mol)	M_w/M_n[a]	DA_{eff}[b] %
16	15600	1.37	
17	15360	1.15	
18	16320	1.17	
19	17630	1.22	92

[a]Determined by GPC (RI detection) in THF at 30°C using PS calibration.
[b]$DA_{eff}\% = [1 - A_{48}/A_0] \times 100$

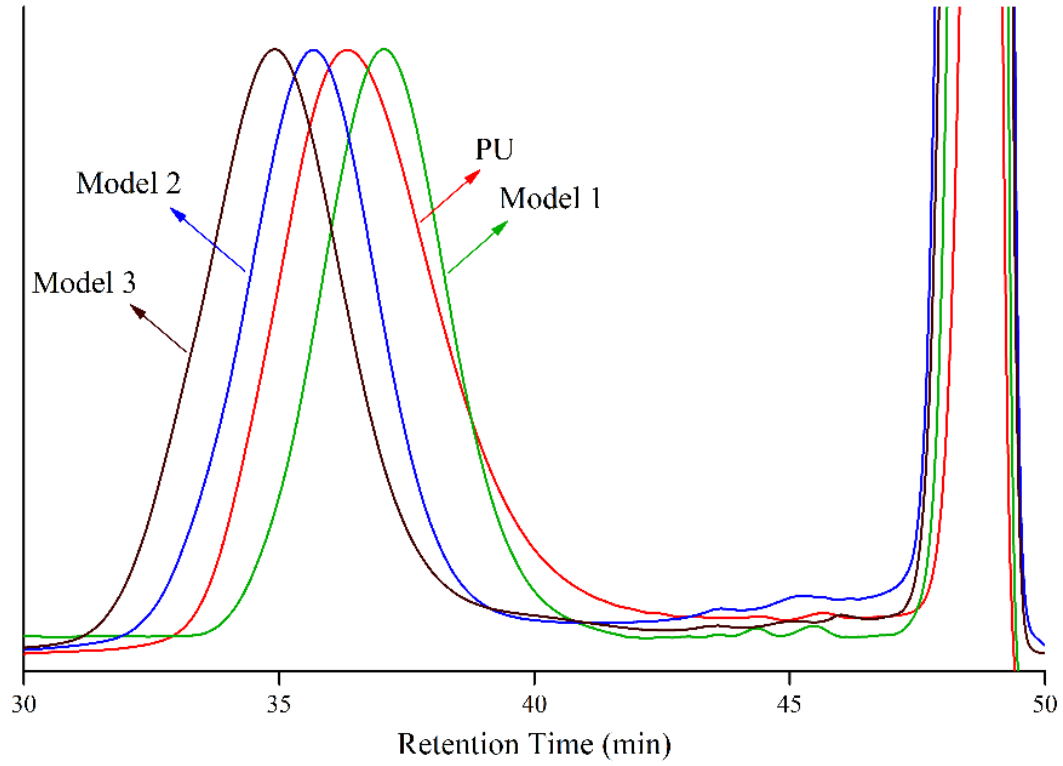


Figure 4.36 : Overlay of GPC traces of compounds **16**, **17**, **18** and **19** in THF at 30°C.

4.7 Modification of PU-(Anthracene-*co*-Alkyne), (15) via Click Reactions

Before preparation of PU-*g*-(PEG-PMMA) a model reaction firs studied to verify the efficiency of CuAAC and DA reaction. For this purpose first CuAAC reaction between PU-(Anthracene-co-Alkyne), **15** and benzyl azide, **5** was conducted in DMF in the presence of CuBr/PMDETA at room temperature for 24 h (Figure 4.37). After the specified time, reaction mixture was diluted with THF, filtered through neutral alumina to remove copper complex, and precipitated in methanol. After these treatments, resulting polymer, **(20)** characterized by ^{1}H NMR and GPC measurements.

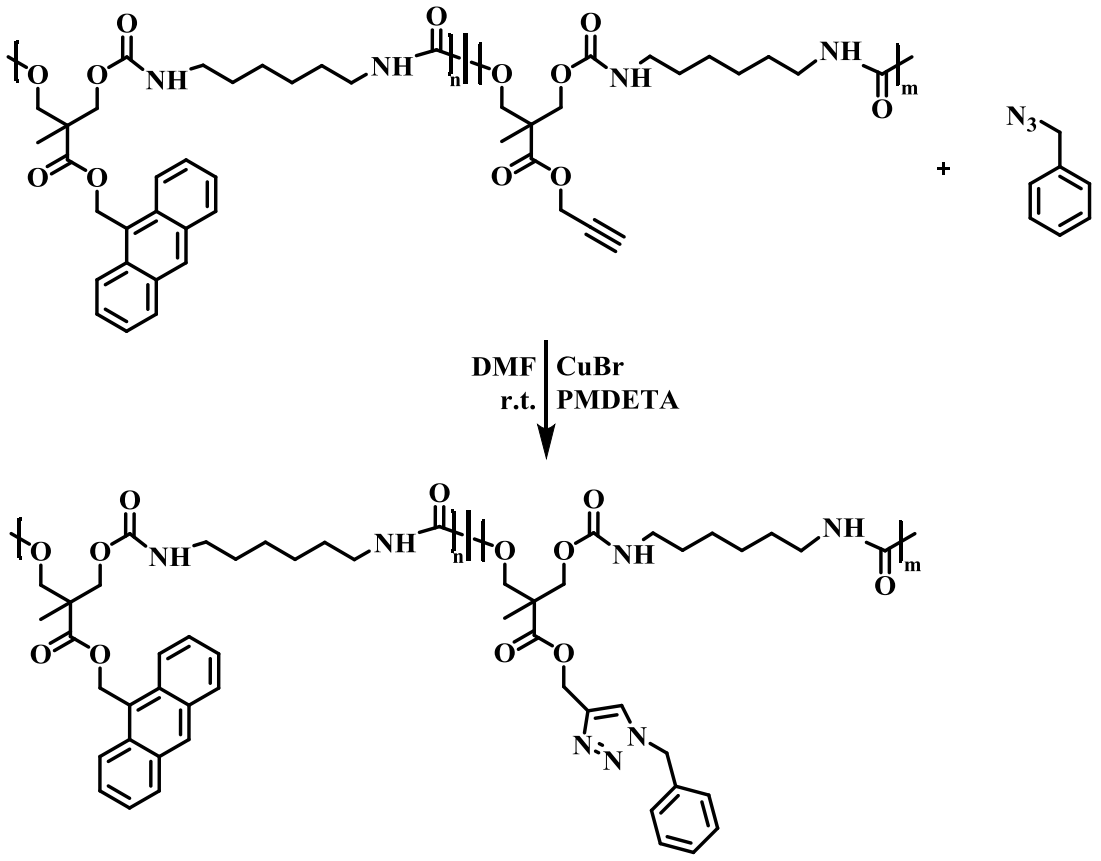


Figure 4.37 : CuAAC click reaction between **15** and benzyl azide.

^{1}H NMR spectroscopy confirmed the expected structure of the compound **20** primarily displaying the characteristic signals of the Ar*H*s of anthracene and methine protons of triazole between 8.50-7.42 ppm, Ar*H*s of benzyl group between 7.39-7.16 ppm, methylene protons adjacent to benzyl group at 5.19 ppm (Figure 4.38). In addition, complete disappearance of methine protons of alkyne at 2.47 ppm and the shift of methylene protons from 4.68 ppm to 5.48 ppm indicates successful preparation of compound **20**. GPC analysis exhibited: $M_{n,\,GPC}$=14380 g/mol, M_w/M_n=1.32 relative to PS standards in THF at 30°C.

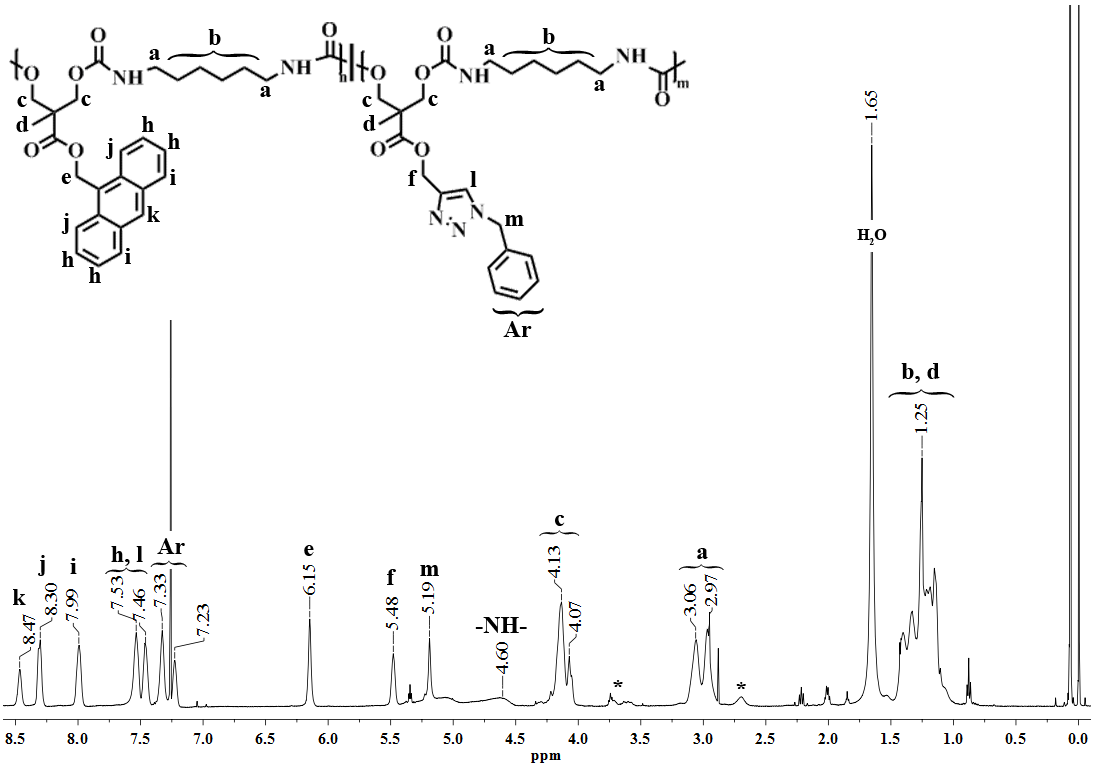


Figure 4.38 : ^{1}H NMR spectra of **20**, in $CDCl_3$.

After CuAAC reaction, DA reaction was performed with **20** and 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.02,6]dec-8-ene-3,5-dione, **2** in dioxane/toluene mixture (2:1, vol/vol) at 105°C for 48 h (Figure 4.39). The DA reaction was monitored by UV-Vis spectroscopy and DA efficiency calculated using absorption of anthracene at 367 nm according to equation **4.1**.

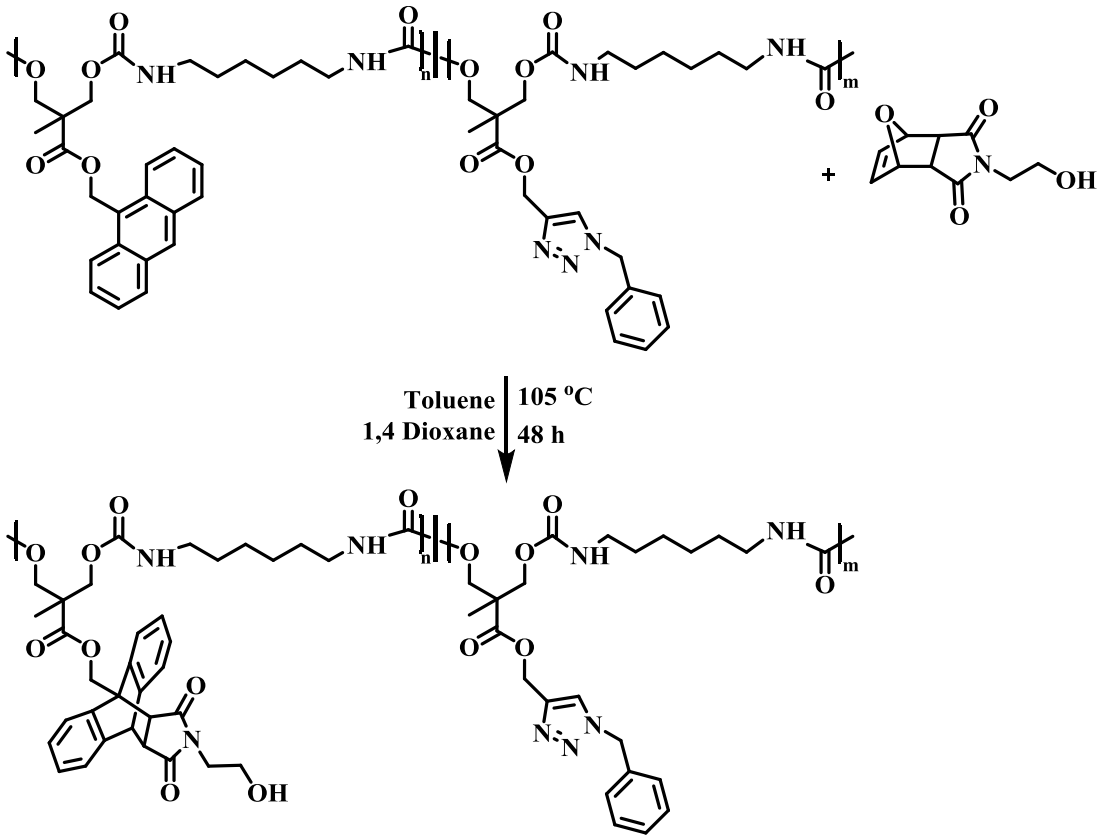


Figure 4.39 : Synthesis of **21** via Diels-Alder reaction.

From the UV-Vis spectroscopy, DA reaction efficiency was found to be 96%, according to maximum absorption values of anthracene at 367 nm (Figure 4.40).

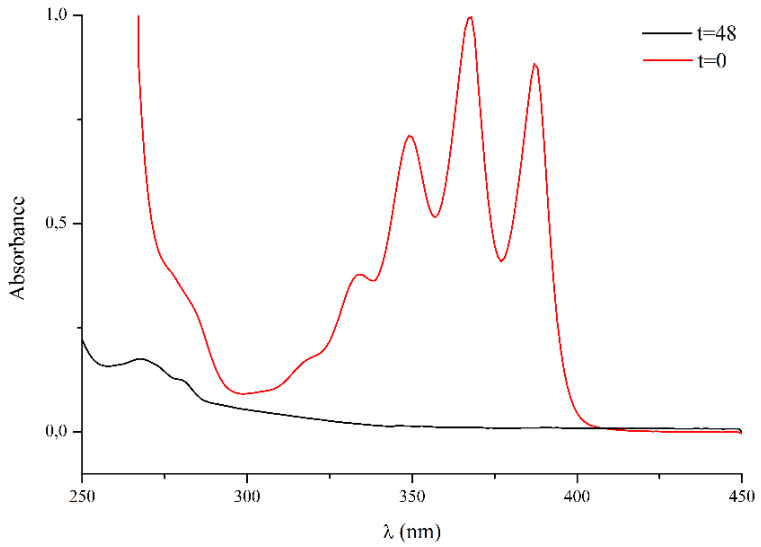


Figure 4.40 : UV-Vis spectra of DA reaction of **20** and **2**.

^{1}H NMR spectroscopy confirmed the expected structure of the compound **21** primarily displaying the characteristic signals of the Ar*H*s of aromatic groups between 7.44-7.08 ppm and methine protons of triazole 7.58 ppm (Figure 4.41). ^{1}H NMR revealed the appearance of new signal regarding methine bridge head protons at 4.77 ppm, the characteristic signals of **2** and Diels-Alder adduct. In addition, ^{1}H NMR spectroscopy of compound **21** confirmed the complete disappearance of Ar*H*s of anthracene between 8.5-7.5 ppm, which indicates successful preparation of compound **19**.

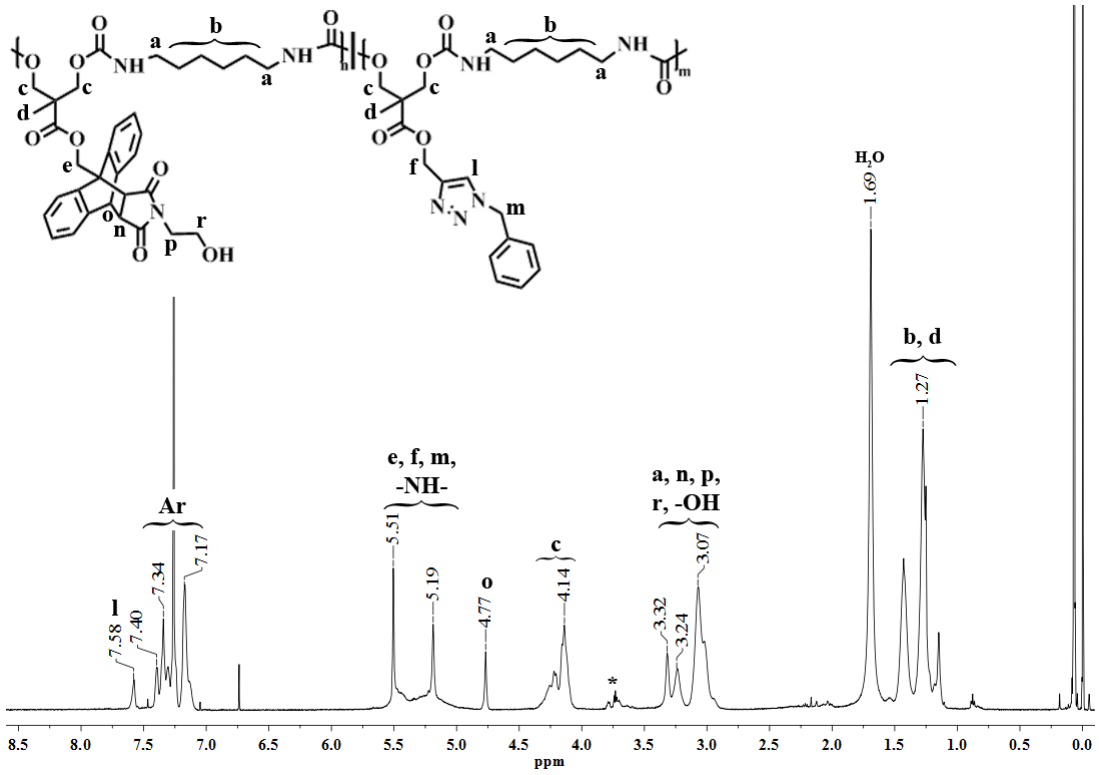


Figure 4.41 : ^{1}H NMR spectra of **21**, in $CDCl_3$.

After CuAAC and DA reactions a clear shift to the higher molecular weight region was detected from GPC measurements while maintaining narrow polydispersity index (M_w/M_n) (Figure 4.42, Table 4.2).

Table 4.2 : The results of PU-(Anthracene-co-Alkyne) modifications.

Polymer	$M_{n,GPC}$[a] (g/mol)	M_w/M_n[a]	DA_{eff}[b] %
15	11088	1.28	
20	14380	1.32	
21	16970	1.25	96

[a]Determined by GPC (RI detection) in THF at 30°C using PS calibration.
[b]$DA_{eff}\% = [1 - A_{48}/A_0] \times 100$

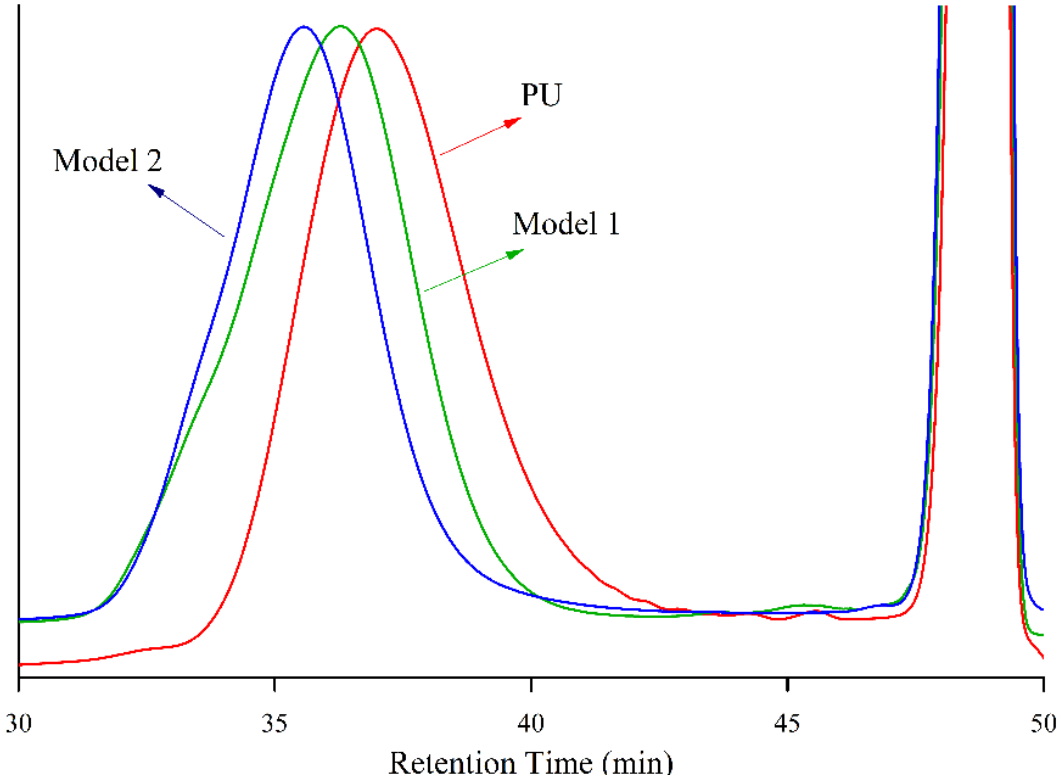


Figure 4.42 : Overlay of GPC traces of compounds **15**, **20** and **21** in THF at 30°C.

Finally, PU-(anthracene-*co*-alkyne) was grafted by Peg-azide and MI-PMMA to obtain PU-*g*-(PEG-PMMA). PU-*g*-PEG was prepared via CuAAC click reaction of PU-(anthracene-*co*-alkyne), **15** and PEG-azide, **7**. **15** and **7** reacted in DMF in the presence of CuBr/PMDETA at room temperature for 24 h (Figure 4.43). After the specified time, reaction mixture was diluted with THF, filtered through neutral alumina to remove copper complex, and precipitated in methanol. After these treatments, resulting polymer, PU-*g*-PEG **(22)** characterized by ^{1}H NMR and GPC measurements.

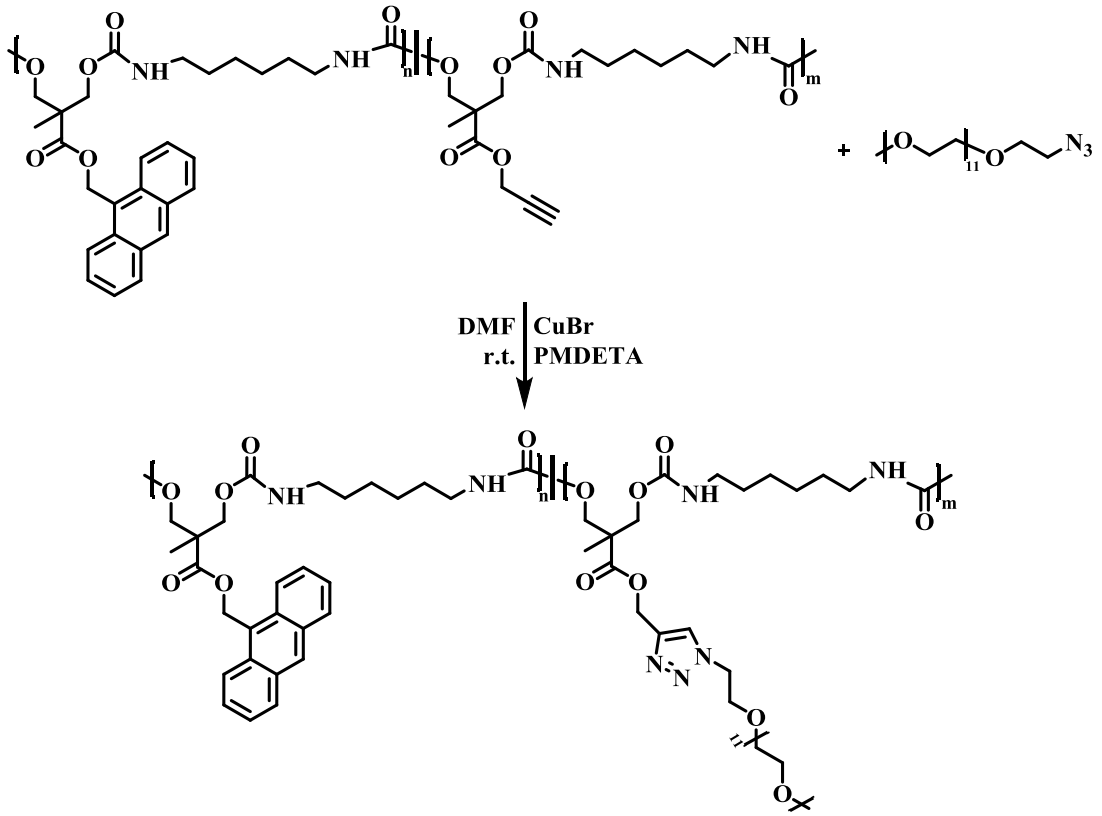


Figure 4.43 : Synthesis of PU-*g*-PEG, **(22)**.

^{1}H NMR spectroscopy confirmed the expected structure of PU-*g*-PEG, **(22)** primarily displaying the characteristic signals of the Ar*H*s of anthracene between 8.53-7.38 ppm and methine protons of triazole at 7.79 ppm (Figure 4.44). In addition, complete disappearance of methine protons of alkyne at 2.47 ppm and the shift of methylene protons from 4.68 ppm to 5.23 ppm, appearance of triazole-CH_2CH_2-PEG protons at 4.51 ppm and 3.85 ppm respectively, methyl protons of PEG at 3.37 ppm and backbone protons of PEG between 3.71-3.50 ppm indicates successful preparation of PU-*g*-PEG. GPC analysis exhibited: $M_{n,\,GPC}$=9200 g/mol, M_w/M_n=1.21 relative to PS standards in THF at 30°C.

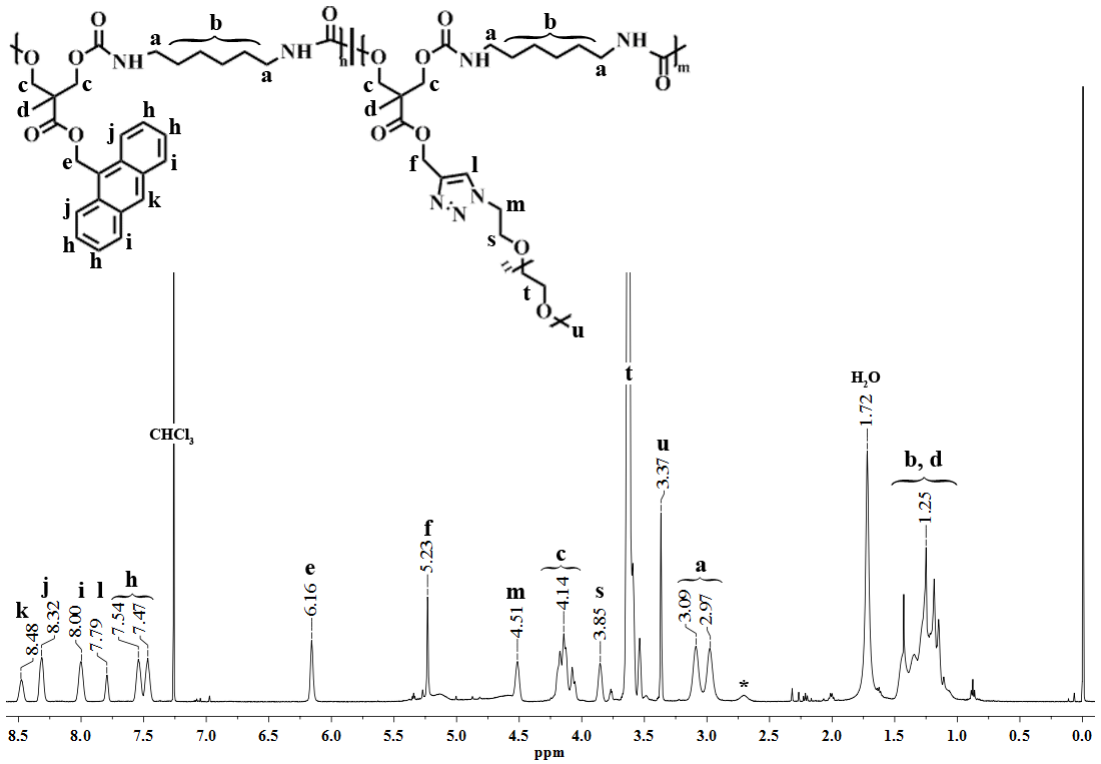


Figure 4.44 : ^{1}H NMR spectra of PU-*g*-PEG, **(22)**, in $CDCl_3$.

Moreover, for the synthesis of PU-*g*-(PEG-PMMA), **(23)**, DA reaction was performed with pendant anthracene functional PU, **22** and MI-PMMA, **4** in dioxane/toluene mixture (2:1, vol/vol) at 105°C for 48 h (Figure 4.45). After the predetermined time product precipitated in methanol/diethyl ether mixture. The DA reaction was monitored by UV-Vis spectroscopy and characterized by ^{1}H NMR and GPC measurements.

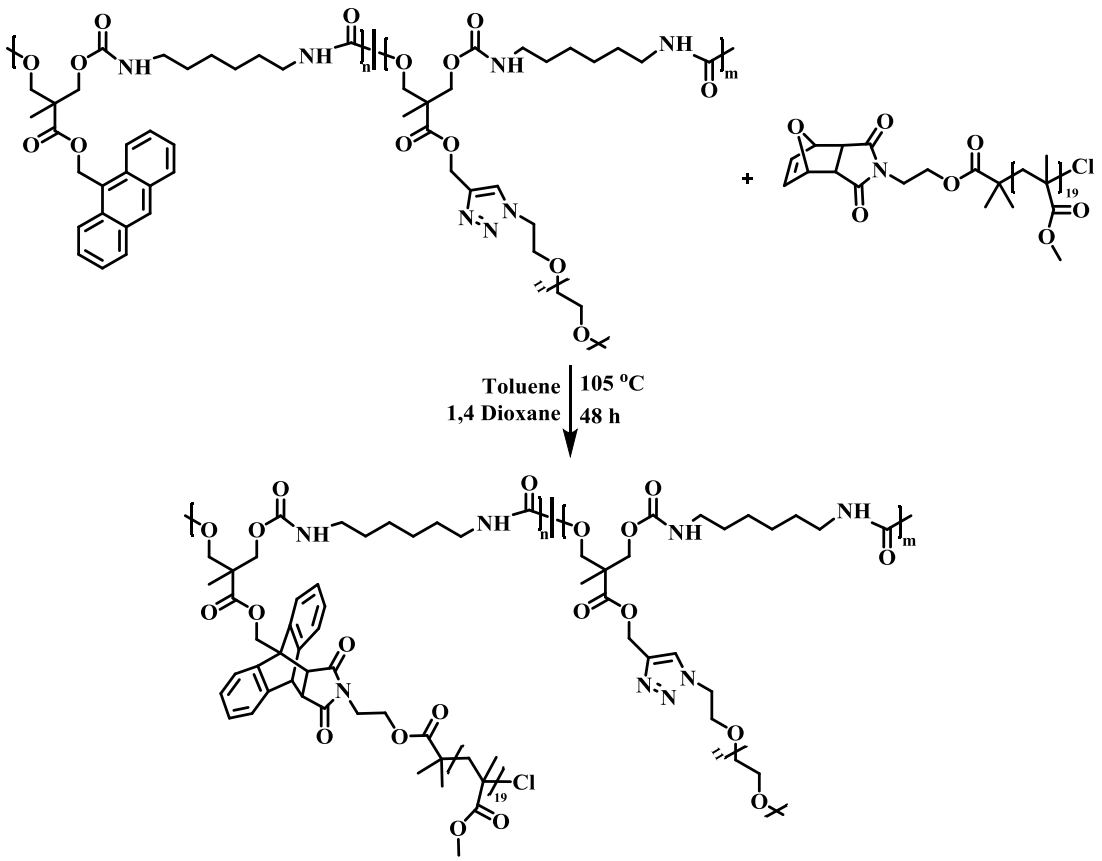


Figure 4.45 : Synthesis of PU-*g*-(PEG-PMMA), **(23)**.

From the UV-Vis spectroscopy, DA reaction efficiency was found to be 95%, according to maximum absorption values of anthracene at 367 nm (Figure 4.46).

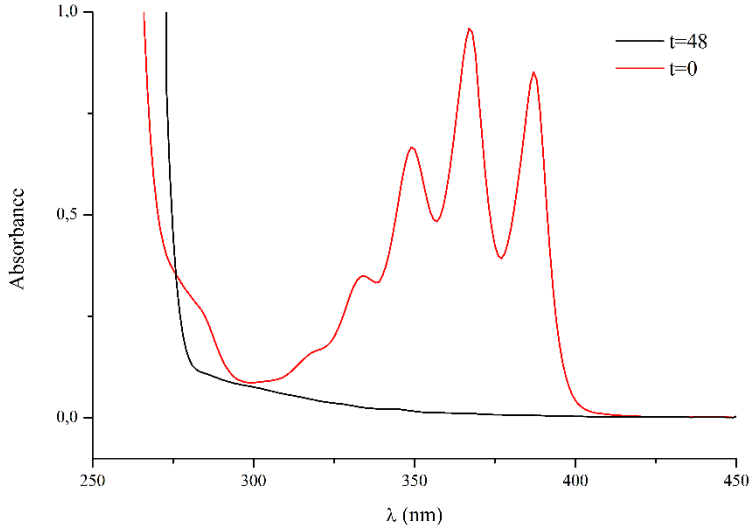


Figure 4.46 : UV-Vis spectra of DA reaction of **22** and **4**.

^{1}H NMR spectroscopy confirmed the expected structure of the compound **23** primarily displaying the characteristic signals of the Ar*H*s of aromatic groups between 7.44-7.07

ppm, methine protons of triazole 7.79 ppm, triazole-CH_2CH_2-PEG protons at 4.52 ppm and 3.86 ppm respectively and backbone protons of PEG between 3.78-3.32 ppm (Figure 4.47). ^{1}H NMR revealed the appearance of new signal regarding methine bridge head protons at 4.76 ppm, the aliphatic proton signals of PMMA and Diels-Alder adduct. In addition, ^{1}H NMR spectroscopy of compound **23** confirmed the complete disappearance of Ar*H*s of anthracene between 8.52-7.42 ppm, which indicates successful preparation of compound **23**.

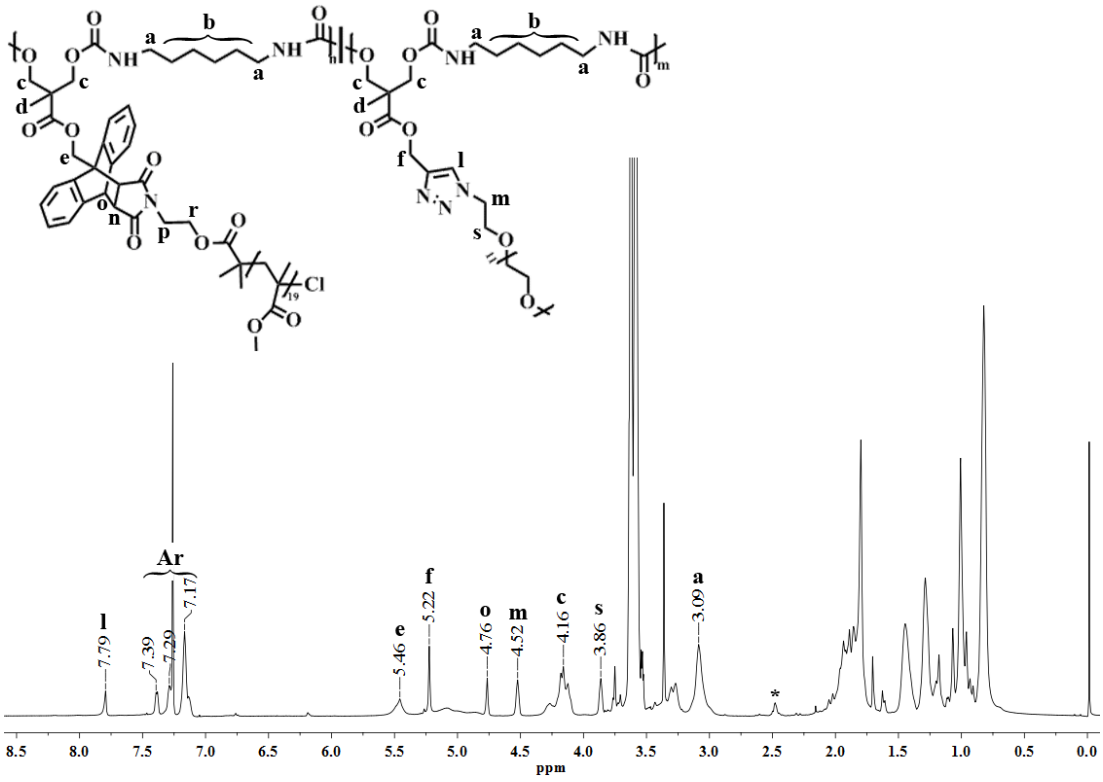


Figure 4.47 : ^{1}H NMR spectra of PU-*g*-(PEG-PMMA), **(22)**, in $CDCl_3$.

GPC measurements of PU-*g*-(PEG-PMMA) are listed below (M_w/M_n) (Figure 4.48, Table 4.3).

Table 4.3 : The results of PU-(Anthracene-co-Alkyne) modifications.

Polymer	$M_{n,GPC}$ (g/mol)	$M_{n,NMR}$ (g/mol)	$M_{n,Theo}$ (g/mol)	M_w/M_n[a]	DA_{eff}[c] %
MI-PMMA	2400[a]	2300	1830	1.12	
PEG-Azide	550[b]	-	-	1.12	
PU	11500[b]	-	-	1.35	
PU-*g*-PEG	8200[b]	-	-	1.17	
PU-*g*-(PEG-PMMA)	10500[b]			1.20	95

[a]Determined by GPC (RI detection) in THF at 30°C using PMMA calibration.
[b]Determined by GPC (RI detection) in THF at 30°C using PMMA calibration.
[c]$DA_{eff}\% = [1 - A_{48}/A_0] \times 100$

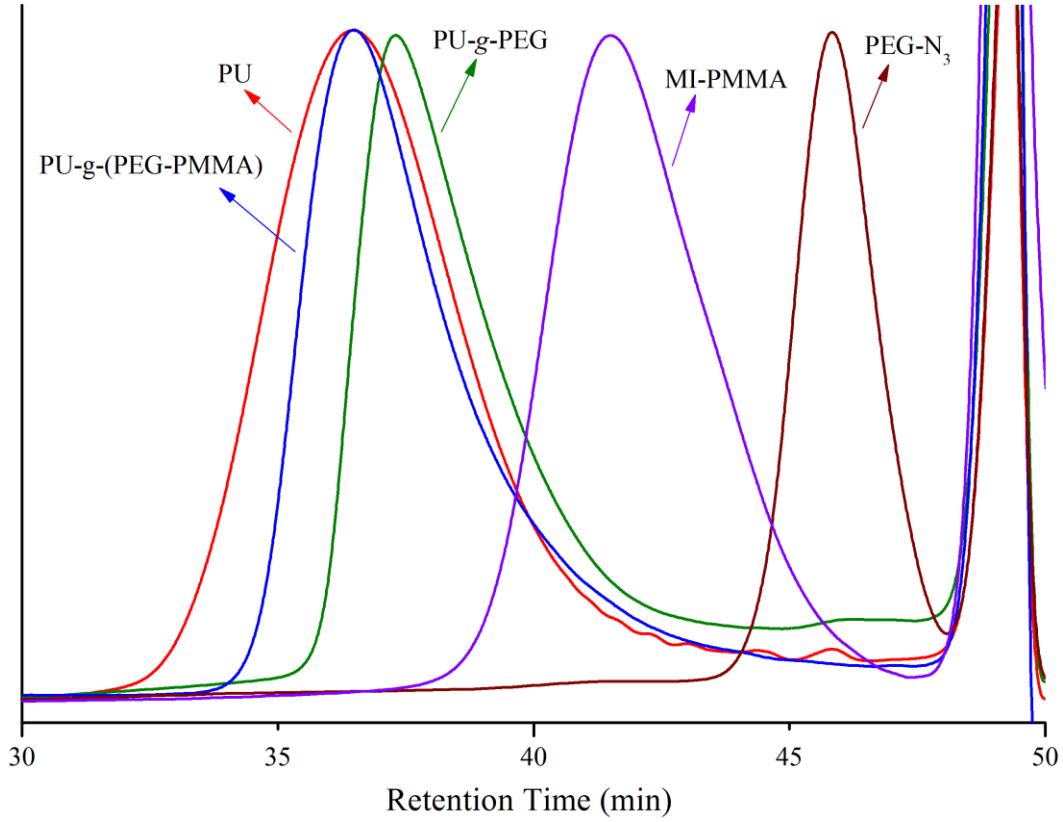


Figure 4.48 : Overlay of GPC traces of compounds **15**, **22** and **23** in THF at 30°C.

5. CONCLUSION

The objective of this thesis was synthesis of different polyurethanes, which have pendant functional groups that suitable for click chemistry, and modification of these polyurethanes with highly efficient click reactions, which have been recently shown to be modular tools for polymer synthesis. In particular, three versatile click reactions, namely the CuAAC, Diels-Alder and active ester substitution reactions.

In first study, alkyne, anthracene and perfluorophenyl ester pendant groups containing PUs were prepared successfully. CuAAC, DA and active ester substitution reactions was used and grafted PU obtained with high reaction efficiency and low polydispersity indexes. The UV, NMR and GPC measurements revealed that CuAAC, Diels-Alder and active ester substitution reactions displayed an efficient and an alternative pathway for modification of PUs.

In the second study, alkyne and anthracene functional groups containing PUs were prepared and PU-*g*-(PEG-PMMA) prepared via double click reactions, namely the CuAAC and DA reactions. CuAAC and DA click reactions were conducted respectively and the PU-graft copolymer obtained with high reaction efficiency and low polydispersity indexes. The UV, NMR and GPC measurements revealed that CuAAC and Diels-Alder reactions displayed an efficient synthetic pathway for modification of PUs.

Consequently, we showed here for the first time that CuAAC, Diels-Alder and active ester substitution click reactions are efficient synthetic approach for the incorporation of a wide variety of linear polymers into the PU main backbone in order to yield PU-graft copolymers.

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